



Synthesis, Characterization and Study of New Mesogenic Compound

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ABSTRACT

Novel compound of rod-like molecules with benzothiazole-aromatic system having an schiff base and ester linkages were synthesised. The structure of synthesised compound was confirmed by using physicochemical techniques such as ¹H-NMR, mass spectra and FT-IR spectra. Differential Scanning Calorimeter (DSC) and Polarizing Optical Microscopy (POM) have been employed to verify their liquid crystalline behaviours and transition temperatures. The compound showed nematic phase only.

Key words: Benzothiazole, Liquid crystal, Schiff Base, Resonance Delocalisation, Mesomorphic.

Abbreviations: DSC: Differential Scanning Calorimetry; POM: Polarised Optical Microscope; NMR: Nuclear Magnetic Resonance

INTRODUCTION

Liquid crystallinity or mesomorphism is a unique state of matter intermediate between a crystalline solid and a regular isotropic liquid. The phenomenon is usually exhibited by long, rod-shaped molecules which contain dipolar groups. It permits molecules to orient along the long axis. Such compounds behave as anisotropic liquids and are birefringent [1].

In chemical research, attempts to correlate compound properties with molecular structure are common. A familiar example is the systematic variation of substituent groups on a physiologically active parent compound to determine how these changes affect activity. Liquid crystalline molecular systems [2-4] have been investigated similarly to ascertain the effects of structural variations on the temperature range over which the mesophase is stable [5].

Interestingly, heterocyclic materials are vital for many optical applications, such as liquid crystal displays [6,7], optical organic transistors [8,9] and biomolecules fluorescent probes [10,11]. These properties are due to their ability to create linear or lateral dipoles and geometrical shapes, which are essential for their optical and electronic properties [12-14]. The presence of electronegative heteroatoms (O,N,S) can significantly impact bond angles, resonance delocalisation, and molecular structure [15-20].

METHODOLOGY

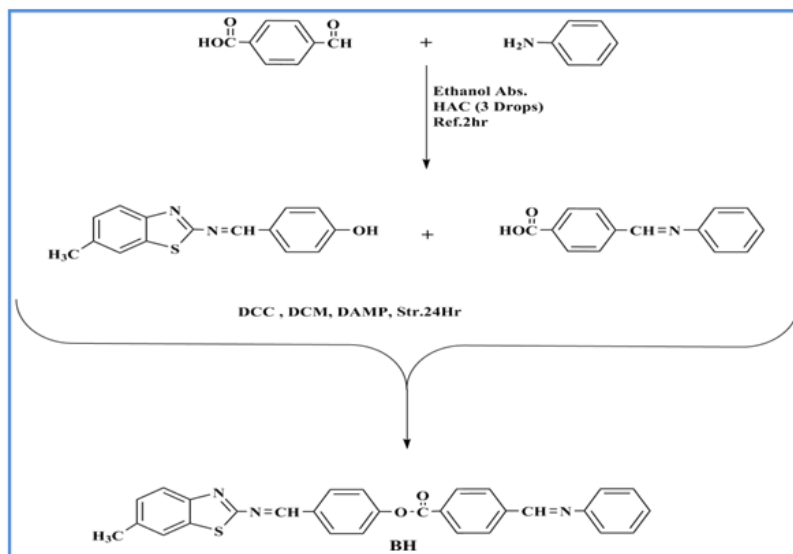
General

Infrared spectra were recorded as KBr pellets on a Buck-M500 spectrometer (Buck Scientific, USA). ¹H and ¹³C-NMR spectra were recorded on a Bruker instrument using CDCl₃ as solvent and TMS as internal standard. Transition temperatures were determined using a Perkin Elmer-Pyris DSC-8000 differential scanning calorimeter with a heating rate of 10°C min⁻¹. The phase transitions were observed with a LeitzLaborlux 12 Pol optical microscope with polarized light in conjunction with a Leitz 350 hot stage (Germany) equipped with a Vario-Orthomat. Mass spectra were recorded on an Agilent technologies 5957C spectrometer.

Synthesis of Schiff bases: One molar equivalent of the appropriately substituted aniline was added to a solution of the appropriate benzaldehyde in ethanol (1:1) to which a few drops of acetic acid were added according to the earlier reported method [41,42]. The mixture was heated under reflux for 2 h and the solid obtained upon cooling was filtered and twice recrystallized from ethanol to give pure compounds (Scheme 2).

Synthesis of 4-(methylthio and methoxy)benzoic acid: 4-Methylthio-benzoic acid or 4-hydroxy-benzoic acid was synthesised according to the literature procedure [43] (Scheme 2) by refluxing 4-mercaptobenzoic acid or 4-hydroxy-benzoic acid, 1-bromomethyl and potassium carbonate in ethanol for 24h. At the end of the reaction, solvent was evaporated and water was added and the aqueous solution was heated to boiling and then cooled to room temperature. A few drops of conc. HCl were added until a solid precipitated. The solid was filtrated and washed with water to afford the target compound (Scheme 2).

Synthesis of esters: Molar equivalents of acids and phenols (0.01 mol) were dissolved in 25 ml of DCM. To the resulting mixture, (DCC, 0.002 mol) and (DMAP, 0.002 mol), were added and the mixture was kept stirring at room temperature for 6h following the reported procedure [44,45]. The precipitated solid (by product) was filtered off and the filtrate was evaporated and the residue was twice crystallised from ethanol (Scheme 2).



Scheme 2: Synthetic routes of the final compound BH

4-(((6-methylbenzo[d]thiazol-2-yl)imino)methyl)phenyl 4-((phenylimino)methyl)benzoate (BH): Chemical Formula: C₂₉H₂₁N₃O₂S; yellow solid; yield 45%; ¹H-NMR spectrum (CDCl₃, 499MHz): δ (ppm) 2.50(s, 3H, CH₃),

7.31-8.48ppm(m,16H,Ar-H), 8.56(s, 1H, CH=N), 9.16(s, 1H, CH=N); ^{13}C -NMR (CDCl_3 , 125MHz): δ (ppm) 21.76 (CH_3),121.09-130.84ppm(Ar-C), 160.37 (CH=N), 164.55 (CH=N), 167.48 (C=O), 174.09 (C=N). IR(cm^{-1}): 3032-3059 (C-H aromatic), 2850-2924 (C-H aliphatic), 1732 (C=O), 1622 (CH=N), 1600 (C=N thiazole), 1448-1587 (C=C aromatic), 1280 (C-O) ; MS (m/z) 475.3 (M^+) (Figure 1).

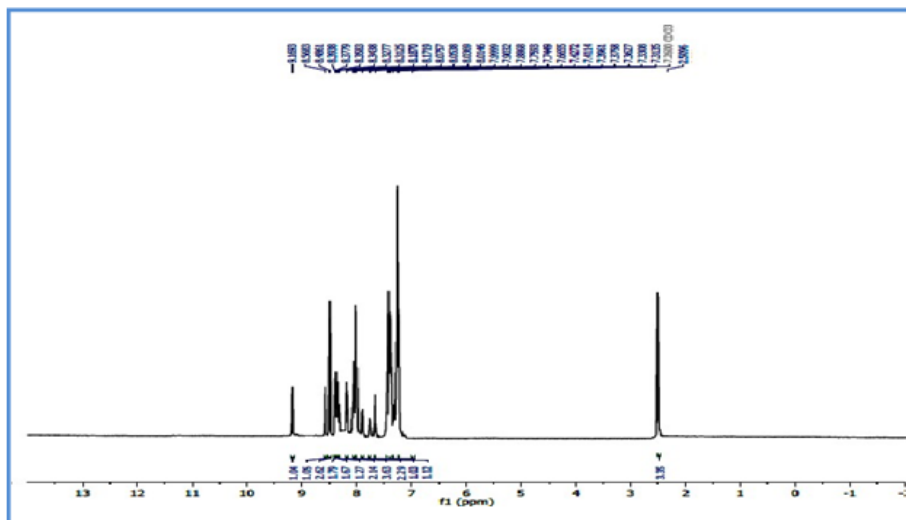


Figure 1: ^1H -NMR for BH

RESULT AND DISCUSSION

Thermodynamic properties (enthalpy and entropy), textures, and the phase transition temperatures of the liquid crystal compound were determined using Differential Scanning Calorimetry (DSC) thermograms and Polarised Optical Microscopy (POM) connected to a hot stage. The DSC heating data and curves of the synthesised molecule (BH) are listed in Table 1.

Table 1: Transition temperatures, corresponding enthalpy values (ΔH , $\text{kJ}\cdot\text{mol}^{-1}$), and entropy changes (ΔS , $\text{J}/\text{mol}\cdot\text{K}$) for the compound BH

C→N	N→I
Comp.	B1H
Transition Temp.($^{\circ}\text{C}$)	205.14
ΔH kJ/mol	31.29
ΔS J/mol. K	65.45
Transition Temp.($^{\circ}\text{C}$)	293.06
ΔH kJ/mol	2.41
ΔS J/mol. K	4.27
ΔT_N ($^{\circ}\text{C}$)	87.92
Note: C: Crystal, N: Nematic, I: Isotropic, ΔT_N : thermal range for nematic phase	

The compound BH Showed nematic phase only with thermal 87.92°C , it is due to the absence of a substituted terminal group at the end of the molecule that might enhance terminal attraction forces and the emergence of

nematic phase [40].

The appearance of the nematic and smectic phase in liquid crystalline compounds depends on the ratio of the terminal and lateral attraction forces specific to the compounds. The nematic phase appears when the terminal attraction force is high, while the smectic phase appears for a lower attraction force [46]. Terminal compensating groups in molecules affect terminal attraction force. Groups with a dipole moment across the molecular axis enhance the terminal attraction forces, and the nematic phase appears. If the dipole moment is across the molecular axis, the molecules follow two arrangements to offset the repulsive forces between similar charges and maintain the parallel arrangement of the particle [46,47]. The molecules tend to be at an angle to diverge similar charges and reduce repulsion in the first order. This arrangement promotes the emergence of the smectic phase. In the second order, the particles take the staggered arrangement (finger arrangement), promoting the emergence of the nematic phase [48,49]. The presence of the benzothiazole group in all compounds has two opposite effects.

CONCLUSION

In this work, we have reported the synthesis and mesomorphic properties of BH, the enantiotropic nematic phase was observed throughout the BH. The first effect enhances the appearance of liquid crystalline properties by increasing molecule polarity due to the two sulphur and nitrogen atoms. The other effect increases molecular width and favours the nematic phase than the smectic phase. The compound BH exhibited nematic phase in a marble texture by heating and schlieren texture on cooling.

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