

FULL PAPER

Supramolecular discotic mesophases containing melamine-core induced by hydrogen-bonding: synthesis and characterization

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The purpose of the presented research is to develop suitable hydrogen-bonding complimentary chemicals to produce melamine-core supra-molecular discotic liquid crystal (LC) materials that can be employed in various applications. We designed and synthesized 3,5di-(3',4',5'tri-alkoxybenzoyloxy) benzoic acid derivatives, one of three types of long-alkyloxy-tailed compounds with unique hydrogen-bonding matching functional groups. The liquid crystalline characteristics were assessed using polarized optical microscopy and DSC. Smectic and nematic phases were discovered.

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KEYWORDS

Melamine; nematic liquid crystal; induced hydrogen bonding.

Introduction

The development regarding new LC materials has piqued attention because of their wide range of applications in microelectronics, particularly for their non-linear optical features and optical data storage capabilities [1-4]. In addition, hydrogen-bonding has been considered an essential interaction in biological and chemical processes. It could create LC in organic compounds with low molar masses [5] and macromolecules. The fundamental driving force behind molecular assembly in such systems is molecular interaction, which has been considered stronger than the van der Waals interactions like ionic interactions, hydrogen bond, and charges transfer interactions, making them eligible to be used in electronics. The hydrogen-bonding interactions, especially, have a considerable effect on intermolecular interactions and thus on the LC's phase behaviors [6].

Furthermore, the H-bond has been considered the most essential non-covalent interactions. It aids in stabilizing the

mesophases by assisting the molecules in aligning their dipole moments in an identical direction, which prevents destabilization resulting from reverse dipoles [7]. Acceptor molecules that have been obtained from pyridine and donor molecules that have been formed from carboxylic acids are widely used in mixes of different hydrogen-bonded molecules that produce liquid crystals. In mesomorphic H-bonded complex formation using 4-n-alkyloxybenzoic acid as a proton donor, such compounds have been utilized as acceptors of the proton. The section aimed to look at phase changes using non-mesogenic proton donors and acceptors.

General experiments

The KBr disc was used to record the FTIR spectra using a Shimadzu Spectrophotometer Model 8300, Japan. KBr pellets from a Perkins-Elmer Fourier-Transform Infrared Spectrophotometer. ¹HNMR spectra have been performed at 300 MHz on a Brüker ACF 300 spectrometer with deuterated DMSO and deuterated Acetone as solvents and TMS as

an internal standard. The Fluka, BDH, and Merck firms provided all of the chemicals utilized in this study (liquid and solid).

Synthesis of 3,4,5-Trialkoxybenzoic acid C1-C3 [8]:

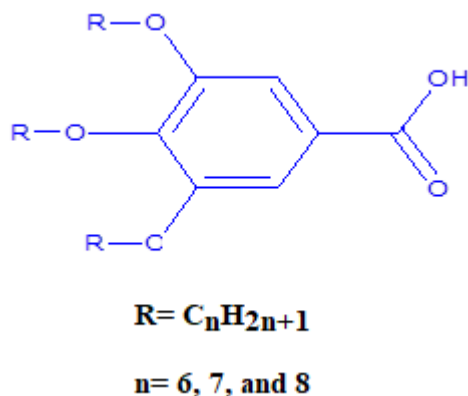


FIGURE 1 Synthesis of 3,4,5-trialkoxybenzoic acid C1-C3

0.01 mole 3,4,5-trihydroxy benzoic acid was dissolved in ethanol of 20 mL, 1.42 gm, 0.03 mole K_2CO_3 was added with constant stirring, and 0.03 mole alkyl bromide (alkyl: 1-hexyl, 1-heptyl, 1-octyl) was progressively added. Overnight, the solution was refluxed. After that, the reaction mixture was heated between (1 and 3) hrs with 1.42 gm, 0.03 mole K_2CO_3 dissolved in a bit of water approximately 5 mL. Furthermore, this solvent was evaporated, and an equivalent water amount was added, followed by heating until the solution was clear. After acidification with concentrated HCl, the solid precipitate was formed (~1 mL).

TABLE 1 Physical properties of 3,4,5-Trialkoxybenzoic acid (C1-C3)

Comp. No.	Molecular Formula	Yield %	b.p °c
C1	$C_{25}H_{42}O_5$	85	202-205
C2	$C_{28}H_{48}O_5$	77	210-212
C3	$C_{31}H_{54}O_5$	63	225-228

Synthesis of 3,4,5-trialkoxy benzoylchloride D1-D3 [9]:

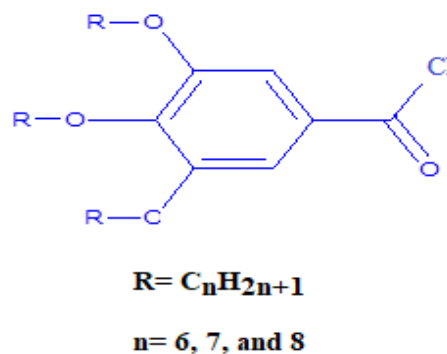


FIGURE 2 Synthesis of 3,4,5-trialkoxy benzoylchloride D1-D3

A mixture of 0.01 mole 3,4,5-trialkoxy benzoic acid (C1-C3), 15 mL thionyl chloride, and a few drops of DMF was refluxed for a period between (3 and 4) hrs. Also, the excess thionyl chloride was evaporated, leaving a dark brown precipitate of 3,4,5-trialkoxy benzoyl chloride as the final product. Furthermore, the leftover acid chloride was utilized with no purification for a subsequent reaction.

General procedure for synthesis of 3,5-di-(3',4',5'-trialkoxy benzoyloxy benzoic acid E1-E3 [10]

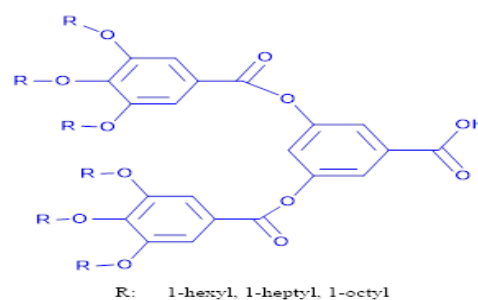


FIGURE 3 Synthesis of 3,5-di-(3',4',5'-trialkoxy benzoyloxy benzoic acid (E1-E3)

A mix which consists of 0.001 mole 3,5-dihydroxybenzoic acid and 10 mL pyridine was added gradually 0.002 mole 3,4,5-trialkoxy benzoyl chloride (D1-D3).

The mixture was stirred at room temperature for 24 h. Then, the mixture poured in ice water for obtaining gray-brown precipitate was filtered.

TABLE 2 Physical properties of 3,5-di-(3',4',5'-trialkoxy benzoyloxy benzoic acid (E1-E3)

Comp. No.	Molecular Formula	Yield %	m.p °c
E1	C ₅₇ H ₈₆ O ₁₂	68	190-193
E2	C ₆₃ H ₉₈ O ₁₂	63	205-208
E3	C ₆₉ H ₁₁₀ O ₁₂	68	230-233

Preparation of the hydrogen-bonded complexes 2,4,6-tris-[3,5-di-(3',4',5'-trialkoxy benzoyloxy benzoic acid (M:E1-3) [11]

R= -C₆H₁₃, -C₇H₁₅ and -C₈H₁₇

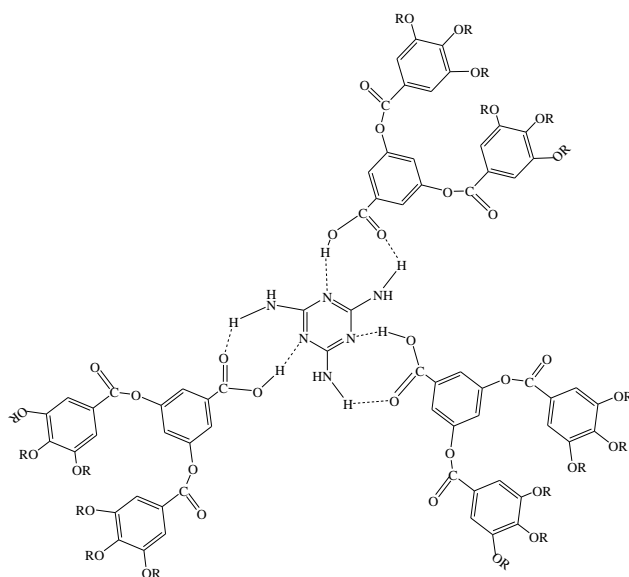


FIGURE 4 Structure of compounds M: E1-3

Slow evaporation related to a dichloromethane solution which contains 3,5di-(3',4',5'-trialkoxy benzoyloxy benzoic acid (E1-E3) as a proton donor and melamine (M) as proton acceptor moieties in a 3:1 molar ratio was used to make the hydrogen-bonded complexes, which were then dried in vacuum at a temperature of 60 Celsius. Furthermore, the solutions have been stirred at room temperature for 24 h, before the evaporation.

TABLE 3 Physical properties of hydrogen-bonded complexes 2,4,6-tris-[3,5-di-(3',4',5'-trialkoxy benzoyloxy benzoic acid (M:E1-3)

Comp. No.	Molecular Formula	Yield %	m.p °c
M:E1	C ₁₇₄ H ₂₆₄ O ₃₆ N ₆	73	83-85
M:E2	C ₁₉₂ H ₃₀₀ O ₃₆ N ₆	72	86-88
M:E3	C ₂₁₀ H ₃₃₆ O ₃₆ N ₆	77	98-100

Results and discussion

The liquid crystals studied in this work were synthesized, as demonstrated in Figure 4. The most extensively employed complementary complexes for the hydrogen-bonding induced supra-molecular discotic LCs are 2,4,6-tris-[3,5di-(3',4',5'-trialkoxy) benzoyloxy] benzoic acid (M:E1-3), which are excellent candidates holding not just hydrogen bond donor (O-H), yet also the acceptor of the hydrogen bond (C=O). Furthermore, most prior, influential observations regarding melamine-derivative mesomorphism have been similarly made in supra-molecular complex systems containing benzoic acid derivatives [13]. Depending on such logic, we mixed 3,5-dihydroxy benzoic acid with 3,4,5- trialkoxybenzoyl chloride - benzoyl chloride (Compound D1-3, Figure 2) in a 2:1 stoichiometry for forming (compounds E1-3, Figure 3), which was after that mixed with melamine in a stoichiometry of 3:1 for forming a mix that has been added to dichloromethane and sonicated till dissolved. The solvent was evaporated, leaving a beige powder studied using ¹H-NMR, FTIR, DSC, and POM.

The prepared carboxylic acid E1-3 was not mesogenic. However, all intermolecular hydrogen bond-induced complexes M: E1-3 had nematic and smectic phases.

FTIR spectroscopy can demonstrate the presence of intermolecular hydrogen bonds in M: E1-3 complexes. E1-3, for instance, has two carbonyl bonds (1731 cm⁻¹ and 1710 cm⁻¹, respectively, corresponding to the ester carbonyl and carboxylic absorptions), while compound M has an

amino group absorption of 3413 and 3329 cm^{-1} . The carboxylic carbonyl band changes to 1718 cm^{-1} and 1705 cm^{-1} for the complexes M: E1-3 because of the establishment of an intermolecular hydrogen bond. The emergence of two broad absorption bands for M: E1-3, centered at 2539 cm^{-1} and 1918 cm^{-1} , is strong evidence for intermolecular hydrogen bonding unionization [14] (Figure 5-7).

$^1\text{H-NMR}$ spectrum data of compound M: E3 revealed singlet signal at $\delta = (9.60-9.63)$ ppm due to (3H, NH) protons and (3H, OH) protons. Signal at $\delta = (7.36-8.17)$ ppm due to (Ar-H) protons, triplet at $\delta = (3.84-4.06)$ ppm which assign to (36H, OCH_2) and multiplet at $\delta = (1.74-2.06)$ ppm (108H, $\text{CH}_2\text{-CH}_2$), triplet at $\delta = (1.64-1.06)$ ppm for the terminal methyl group (54H, CH_3) (Figures 8-10).

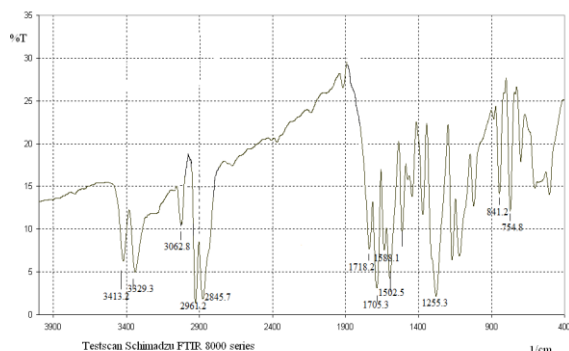


FIGURE 5 FTIR spectrum of compound M: E1

Polarized microscopy was used to explore the phase transition temperatures of E1-3 (Figure 7). Enantiotropic liquid crystals make up all of the E1-3 complexes. Furthermore, compound E1 exhibits nematic phases with an oily-streak texture that changes color when heated and focal-conic textures when cooled [15]. In contrast, compounds E2-3 have a smectic C phase with a silk texture.

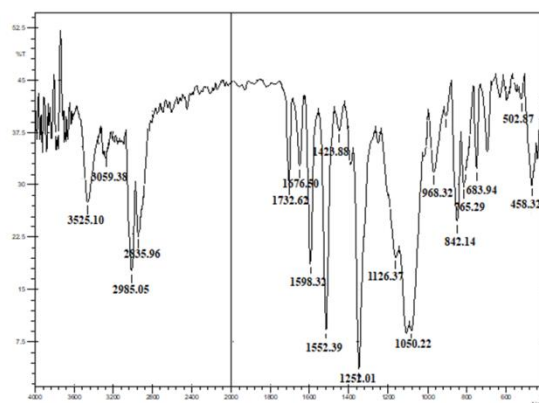


FIGURE 6 FTIR spectrum of compound M: E2

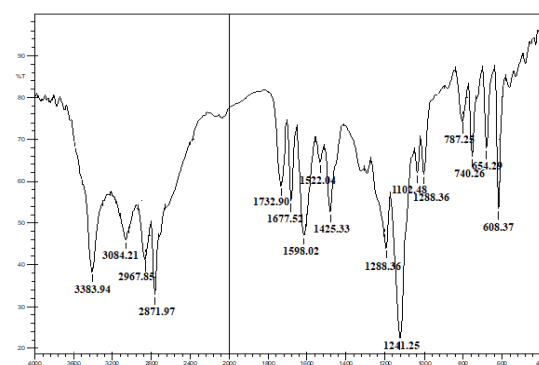


FIGURE 7 FTIR spectrum of compound M: E3

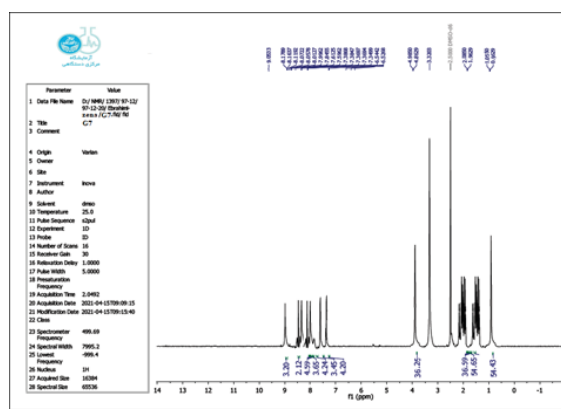


FIGURE 8 $^1\text{H-NMR}$ spectrum of compound M: E1

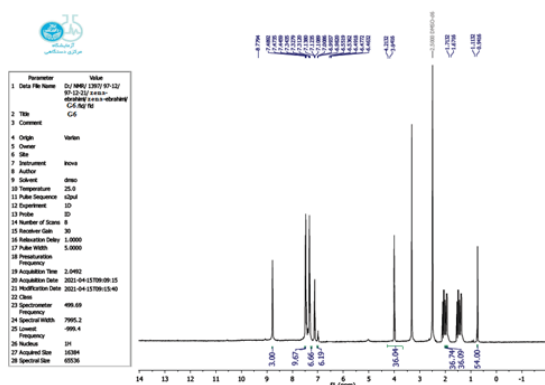


FIGURE 9 ^1H NMR spectrum of compound M:E2

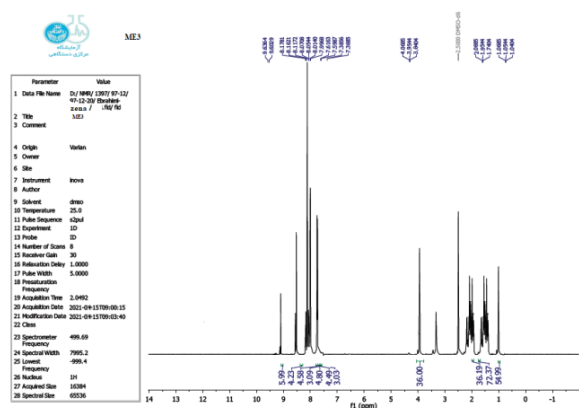


FIGURE 10 ^1H NMR spectrum of compound M:E3

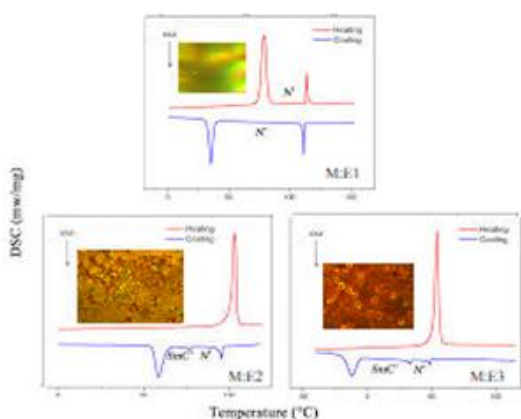


FIGURE 11 DSC thermogram and POM texture of compound M:E1-3

Conclusion

Melamine-benzoic acid derivative complex 2,4,6-tris-[3,5-di-(3',4',5'-trialkoxy benzoyloxy) benzoic acid (M:E1-3), are the most widely used complementary

compounds for hydrogen-bonding induced supramolecular discotic LCs. All of the E1-3 complexes are enantiotropic liquid crystals. Compound E1 exhibits nematic phases, revealing an oily-streak texture with color-changing heating and showing focal-conic textures by cooling. In contrast, compounds E2-3 display a smectic C phase with a silk texture.

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