

e-ISSN: 2319-8753 | p-ISSN: 2320-6710

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International Journal of Innovative Research in SCIENCE | ENGINEERING | TECHNOLOGY

INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

808

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 10, Issue 6, June 2021

INTERNATIONAL STANDARD SERIAL NUMBER INDIA

Impact Factor: 7.512

9940 572 462

6381 907 438

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| e-ISSN: 2319-8753, p-ISSN: 2320-6710| <u>www.ijirset.com</u> | Impact Factor: 7.512|

|| Volume 10, Issue 6, June 2021 ||

[DOI:10.15680/IJIRSET.2021.1006377]

Investigations on Mesogenic 10BA:TMD (p-Decyl Benzoic Acid:O-Toluamide)

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ABSTRACT: The phase characterization by characteristic textural observations of the newly synthesized hydrogen bond mesogen compound 10BA:TMD containing mesogen *p*-decyl benzoic acid (10BA) and non-mesogen *ortho*toluamide (TMD) using polarizing optical microscope (POM) attached with camera and laboratory fabricated hot stage is carried out,. The study reveals that the compound 10BA:TMD exhibits enantiotropic induced smectic G phase and quenching of nematic phase due to formation of hydrogen bond. DSC study gives the phase transition temperatures confirming POM studies. FTIR and Proton NMR studies also confirmed the hydrogen bond formation.

KEYWORDS: Intermolecular interactions, hydrogen bond, Fourier Transform Infrared Spectroscopy. POM, Differential Scanning Calorimetry, Proton Nuclear Magnetic Resonance

I. INTRODUCTION

The attention has been focused on the mesomorphism induced by the non-covalent electrostatic interaction involving intermolecular hydrogen bonding. The significance of hydrogen (H-) bonded mesogens (liquid crystal materials) is all together highly realized. It was found that hydrogen bonds are successfully employed for the formation of new mesophase(s). The hydrogen bond has a striking influence on the phase behaviour as well as transition temperatures. The hydrogen bond liquid crystal (mesogen) may be synthesized with the combination of mesogen + mesogen, mesogen + non- mesogen and non- mesogen + non- mesogen but the present work is containing mesogen p-decyl benzoic acid (10BA) and non-mesogen *ortho*-toluamide (TMD)..

II. RELATED WORK

Since reported literature is vast, a very brief related work is given. Previous work on liquid crystals, self assembled liquid crystals and supramolecular liquid crystals through hydrogen bonding were discussed [1,2] and in particular Poleos et al [3] reviewed the literature covering all aspects. Supramolecular liquid crystals were thoroughly reviewed [4]. Preparing novel liquid crystals involve various techniques like synthesizing using organic compounds and mixing two different compounds, metals and halogenated compounds etc were found [5,6]. The non-covalent interactions exhibit significant effects on physical and thermal properties i.e., mesomorphic behaviour and transition temperatures [7]. Induced smectic A phase is reported [8] in p-n-alkyl benzoic acids with p-(p'-octyloxy benzylidene)-cyano aniline. A new series of supra molecular liquid crystals ($nOBA:TMD \ n = 4$ to 12) were studied by Kalyani et al. [9]. Supramolecule through intermolecular hydrogen bond in 50BA:TMD liquid crystal was studied [10]. Quenching of old phases, inducement of new phases and change in transition temperatures in the prepared complexes were identified which has helped us to conclude that certainly intermolecular Quenching of old phases, inducement of new phases and change in transition temperatures in the prepared complexes were identified which has helped to conclude that certainly intermolecular Quenching of old phases, inducement of new phases and change in transition temperatures in the prepared complexes were identified which has helped to conclude that certainly intermolecular MD [11-14].

III. EXPERIMENTAL

p- decyl benzoic acid (10BA) which is a mesogen and non mesogen o-toluamide (TMD) were supply by M/s Frinton laboratories, Inc., USA. Solvent pyridine was supply by Qualigens India. The complex, *p*-decyl benzoic acid : p-toluamide (10BA: TMD) was synthesized by refluxing together in equimolar ratio (1:1) of *p*- decyloxy benzoic acid (0.68717 gm) and toluamide (0.40551 gm). They are taken individually and mixed in the pyridine solvent (20ml). Now the two solutions are mixed and kept under constant stirring at 80°C for ~4hrs. Then most of the pyridine is removed by vacuum distillation process. It means the volume of the resultant homogeneous mixture was reduced to



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|| Volume 10, Issue 6, June 2021 ||

|DOI:10.15680/IJIRSET.2021.1006377|

almost dryness by removing the excess pyridine under a controlled vacuum filtration. The white crystalline product was dried and re-crystallized from hot dichloromethane solution. The yielding is at about 85%. FTIR 5300 spectrometer of JASCO (Japan) instrument is used. Spectra are taken in solid KBr and liquid chloroform. Russel Hertel polarizing microscope with a heating stage is used to identify the different phases and to determine transition temperatures. Universal camera attachment with computer is also used for taking the photographs of different textures. A digital thermometer with the range -50° C to 300° C and with an accuracy of $\pm 0.1^{\circ}$ C is used to determine the temperature. The transition temperatures of the compounds under investigation were determined using Perkin-Elmer DSC, modal Diamond and the samples were measured with single pan balance Metler Model AE 240 with an accuracy of 0.01mg. The ¹H NMR spectra were recorded on the Brucker Avance 400 MHz instrument and chemical shifts in CDCL₃ were given in ppm.

IV. RESULTS AND DISCUSSION

A novel mesogen containing mesogen *p*-decyl benzoic acid (10BA) and non-mesogenic *ortho*-toluamide (TMD) was synthesized and further characterized as given below.

FTIR Spectral Studies:-

The Fourier transform infrared spectral studies are performed both for the free mesogen, non-mesogen and hydrogenbonded complex. The chosen combination includes mesogenic compound *p*-*n*-decyl benzoic acid (10BA) and the non mesogenic (TMD) *ortho*-toluamide and hydrogen bonded 10BA:TMD. The properties of the compounds with their relevant specifications are summarized in Table 1 and associated structures illustrated in Figures 1, 2 and 3.

Table 1: Relevant sp	pecifications of	10BA and TMD
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Compound	Molecular Weight (gms)	Chemical Formula
<i>p</i> -decyl benzoic acid(10BA)	262.39	$C_{17}H_{26}O_2$
<i>o</i> -Toluamide (TMD)	135.17	C ₈ H ₉ NO



Fig.1: Molecular Structure of *p*-decyl benzoic acid





Fig.3.Structure of Inter Molecular Hydrogen bonded Mesogen 10BA:TMD



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The role of intermolecular hydrogen bonding is explained with wavenumber assignments as shown in Table 2 and 3 of non-mesogen, mesogen and hydrogen bonded mesogen that convinced the initiation of smectic G phase is examined with shift in the wavenumber of the bonds where absorption and emission of radiation exists. The FTIR spectra are given in Fig. 4.



The band are assigned to functional groups and shown in Table 2. And significant bands are shown Table 3.

Compound	TMD	10BA	10BA:TMD	Compound	TMD	10BA	10BA:TMD
Functional				Functional			
Group				Group			
(NH) _{ASY}	3367		3366	O-H		2923	2851
(NH) _{SY}	3185		3184	(CH) _{IPB}		1518	
C=O	1655	1683	1658	(OH) _{IPB}		1422	
(NH) _{IPB}			1610	(COC) _{SY}		1179	
C-N	1394		1422	(COC) _{ASY}		1015	
C-0	1137	1290	1289	(OH) _{OPB}		945	944
(NH) _{OPB}	682		694	C-C		857	

Table 2: Solid state IR Spectral Data of TMD, 10BA & 10BA: TMD (cm⁻¹)

Table 3 : Solid State Infrared Spectra of 10BA, TMD and 10BA: TMD of significant functional groups

Compound	(NH) _{ASY}	(NH) _{SY}	(OH) _{ACID}	(C=O) _{ACID}	(C=O) _{AMIDE}	(NH) _{OPB}
10BA			2923	1683		
TMD	3367	3185			1655	682
10BA:TMD	3366	3184	2851	1658	1610	694

These variations in chemical shifts indicate the involvement of the OH group of acid and the NH group at the tail end. The hydrogen bonding is expected between the involved groups by self assembling process leading the small molecular aggregates to form lamellar texture. The larger variations emphasis the local field variations within the molecule to change the order of transition and the large tilt angle in inducement of smectic G phase. From observations of stretching frequencies of $(C=O)_{amide}$, $(OH)_{acid}$ and NH, the hydrogen bonding may be expected between $(C=O)_{amide}$ and $(OH)_{acid}$ that lead to structure as illustrated in Figure 5. The IR spectra of the complexes were recorded in chloroform, which reveal the increased stretching frequencies of (OH) resulting in the destruction of hydrogen bonding in solution.

From the theoretical considerations, using SPARTAN [30] software, the structures of 10BA, and TMD were obtained. Then the hydrogen bonded 10BA:TMD molecular structure was obtained theoretically (Fig. 5). Using the same software, the FTIR spectral absorption bands in wave numbers were obtained for the associated functional groups of the studied compounds and the shifts are tabulated in Table 4. From the Table 3 and 4, it is observed that the



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experimental and theoretical shifts are in reasonable agreement and hence the formation of hydrogen bond is confirmed.

Table 4: FTIR analysis for the non-mesogen, mesogen and hydrogen bonded mesogen TMD, 10BA and 10BA:TMD. (in cm⁻¹)

Com-		(NH) _{opb}		(C=O) _{acid} (C=O) _{amide}			(OH) _{acid}								
pound	T (AM	1)	EX	P.	T (AN	M 1)	EXI	2.	T (AN	M1)	EX	P.	T (AN	M 1)	EXI	Р.
TMD	3530	47	682	12					1999	22	1655	45				
10BA					2075	19	1683	25					3427	84	2923	72
10BA:	3483		694		2056		1658		1977		1610		3342		2851	
TMD																



10BATMD10BA:TMDFig 5. Structures(Black- carbon, Red- oxygen, Violet – nitrogen, White – hydrogen)

Polarizing optical microscopy studies: -

From POM studies, various textures related to different phases are shown in Fig. 6. On heating cycle, the pure 10BA exhibits nematic phase in between the temperatures 97.2°C and 107.4°C. Afterwards, on further heating, it becomes isotropic above 108.8°C. In cooling cycle, the nematic droplets separated from the isotropic phase at 103.5°C combine to form nematic schliren phase at 97.3°C and this phase remains up to 88.9°C and becomes solid below 88.9°C. The transition temperatures corresponding to pure 10BA supplied by the manufacturer, M/s Frinton Laboratories are also given. i.e., the pure 10BA exhibits nematic phase in between the temperatures 94.5°C and 109°C. On further heating, it becomes isotropic. The pure TMD is a non mesogen. The synthesized complex 10BA: TMD exhibits Smectic G phase in between solid phase and isotropic phase. The pure compound 10BA exhibits threaded nematic texture. The hydrogen bonded complex 10BA: TMD exhibits an induced smectic G phase both in heating and cooling cycles. In heating, smectic G phase is observed in between the temperatures 75°C and 83°C. On cooling, Smectic G phase appears directly after Isotropic phase at 83°C. The smectic G phase consists of mosaic like structure. The smectic G phase is changed to solid phase below 75°C. Hence the synthesized complex exhibits enantiotropic liquid crystal nature with inducement of smectic-G phase and without nematic phase. Inducement of new phase and/or quenching of existing phase is a striking manifestation of hydrogen bond formation. The data is depicted in Table 5.



Nematic phase of 10BA

Solid phase of 10BA

Solid phase of 10BA:TMD Smectic G phase of 10BA:TMD

Fig. 6. Textures at different phases



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Differential Scanning Calorimetry studies:-

The transition temperatures of pure 10BA and the synthesized compound 10BA: TMD according to the Differential Scanning Calorimetry (DSC) are given below.

In heating cycle, the pure 10BA exhibits nematic phase at 96.7 °C and this phase extends up to 107.5 °C to change to isotropic phase. In cooling cycle, the nematic phase separates from the isotropic phase at 103.9 °C and this phase remains up to 93.3 °C and becomes solid. The DSC thermogram of 10BA is shown in Fig. 7 in both heating and cooling cycles. In heating cycle, 10BA:TMD exhibits smectic G phase in between temperature 73.42 °C and 79.6 °C. Afterwards, on further heating, it becomes isotropic. In cooling cycle, smectic G phase exists in between the temperatures 77.8 °C and 70.53 °C. Afterwards, on further cooling, it becomes solid below 70.53 °C. The DSC thermogram of 10BA: TMD is shown in Fig. 8 in both heating and cooling cycles at a scan rate of 5 °C/min.

The transition temperatures obtained from the DSC studies are shown in Table 6. The phase transition temperatures observed through thermal polarizing microscope are almost coinciding with DSC studies.



Fig. 7: DSC Thermogram 10BA

Fig. 8: DSC Thermogram of 10BA:TMD

	1	0BA		10BA:TMD					
Study	Expt	Solid to N	N to Isotropic	Study	Expt	Solid to S _G	S _G to Isotropic		
Frinton Labs		94.5 °C	109 ⁰ C						
Present	T.M (H)	96.7 ⁰ C	107.5 [°] C		T.M (H)	78°C	89.7°C		
	T.M(C)	93.3 [°] C	103.9 [°] C	Present	T.M(C)	76.8°C	86.5°C		
	DSC(H)	96.1 °C	107.5 °C	Tresent	DSC(H)	91.35(0.958)	Peak not resolved		
	DSC(C)	93.3 °C	103.98 °C		DSC(C)	70.53 (0.736)	77.8 (1.41)		

Table 5. DSC and TM data on

H – Heating; C – Cooling

(enthalpy value)



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Proton Nuclear Magnetic Resonance (NMR) studies:

Nuclear magnetic resonance (NMR) spectroscopy uses high magnetic fields and radio- frequency pulses to manipulate the spin states of nuclei—including ¹H and ¹³C that have nonzero- spin angular momentum. For a molecule containing such nuclei, the result is an NMR spectrum with peaks whose positions and intensities reflect the chemical environment and nucleic positions within the molecule. Proton NMR spectra of compounds are given in Fig.9.



Proton NMR OF 10BA:TMD

Fig. 9: Proton NMR spectra



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Consider the labeled molecular structure **Fig.10** of hydrogen bonded mixture that reveal chemical shifts the CH₃ stretching with triplet (3H)around chemical shift $\delta = 0.9$ labeled as **a**, the CH₂ stretching with quartet(2H) around chemical shift $\delta = 1.25$ labeled as **b** the CH₂ stretching with multiplet (14H) around chemical shift $\delta = 1.63$ labeled as **c**,



Figure 10. Structure of Hydrogen bonded 10BA: TMD

the CH₂ stretching with triplet (2H) around chemical shift $\delta = 2.65$ labeled as **d**, the CH₃ stretching with singlet 3H)around chemical shift $\delta = 2.51$ labeled as **e** and broad NH₂ around 5.9 associated with the stretching's of the aromatics of both the involved groups with multiplets ranging from 7.2 to 7.5.Further studies of toluamide exhibit CH₃ stretching around 2.45 singlet and narrow NH₂ of 5.85. From the proton NMR studies of the hydrogen bonded complex all the peaks are fitted well to the hydrogen bonded structure with the NH₂ of toluamide at 5.85 is shifted to 5.9 with reduced intensity due to hydrogen bonding associated with variation in the CH₃ peak of toluamide. These studies reveal downward shift of 0.5ppm due to hydrogen bonding.

The relative variation of chemical shifts of all the three small molecules depicts the formation of hydrogen bonding between the free individuals in contrast with chemical shifts lying between either individual. The structure is elucidated with hydrogen bonding between the COOH group and the NH group of toluamide that fetch with the contribution with the aromatic protons and with broad NH and reduced intensity between the two small molecules. The variations in chemical shifts due to carboxylic acid protons, the vital role of CH stretching's predominated by OH that influenced hydrogen bond formation. The Variation in chemical shifts show down field shift which signify inter molecular hydrogen bond formation.

V. CONCLUSIONS

From the present study it is noted that the transition temperatures are reduced in 10BA:TMD mesogen compared to 10BA. The 10BA:TMD mesogen shows enantiotropy nature of smectic G phase. The textural study reveals quenching of nematic phase and inducement of smectic G phase manifests the formation of hydrogen bond in 10BA:TMD The intermolecular hydrogen bonding is convinced the anisotropic nature of the material with variations in stretching frequencies attributed by FTIR spectra. The structural confirmation through NMR spectrum of bonded mesogen is attributed with both the free compounds with chemical shifts in their specified range. The smectic G phase obtained by cross linkage between the two small molecules with increased molecular weight possesses high thermal stability and restricted melt flow. The theoretical studies provided by SPARTAN also confirm the experimental results of H-bond in 10BA:TMD.

VI.ACKNOWLEDGEMENTS

The authors gratefully acknowledge Major Research Project No.F:34-12\2008 (SR) dated 30 DEC 2008 and one of the author (SSS) is grateful to UGC New Delhi for providing BSR Faculty fellowship No.F4-5(11)/2019(BSR) Dt.17-8-2020.

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| e-ISSN: 2319-8753, p-ISSN: 2320-6710| <u>www.ijirset.com</u> | Impact Factor: 7.512|

|| Volume 10, Issue 6, June 2021 ||

DOI:10.15680/IJIRSET.2021.1006377

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