

Synthesis and Spectroscopic Characterization of bis-Swallow Tailed Mesogen

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Abstract: This paper includes Synthesis of liquid crystalline compounds derived from Di- and Tri-hydroxy benzoic acids with bis-swallow tailed which called *N,N'*-1,4-phenylbis[3,5-Di(*p*-alkoxybenzoyl) benzamide] and *N,N'*-1,4-phenylbis[3,4,5-Tri(*p*-alkoxybenzoyl) benzamide], and study the effect of these ends on the mesogenic properties. The synthesized compounds were characterized using FT-IR, CHNS analysis and ¹H-NMR. The liquid crystalline properties of the prepared compounds which were verified using differential scanning calorimeter (DSC) and hot-stage polarizing optical microscope (POM) were discussed.

Keywords: Liquid crystalline phase, Thermotropic, Lyotropic

1. Introduction

Liquid crystals (LCs) are substances that exhibit a phase of matter that has properties between those of a conventional liquid, and those of a solid crystal⁽¹⁾. Liquid crystals exhibit different molecular arrangements than the liquid and solid states. The liquid crystalline state may result either from the heating of solids (thermotropic liquid crystals) or from the action of certain solvents or solids (lyotropic liquid crystals). Liquid crystalline phases represent intermediate states and are also called mesophases⁽²⁾.

2. Characterizing Liquid Crystals:

The following parameters describe the liquid crystalline structure:

- 1) Positional Order.
- 2) Orientational Order.
- 3) Bond Orientational Order.

Each of these parameters describes the extent to which the liquid crystal sample is ordered⁽³⁾.

Liquid Crystals Phases:

- 1) **Nematic phase** (derived from the greek word "Nema" meaning thread like)⁽⁴⁾.
- 2) **Smectic Phase** (originates from the Latin word "smecticus", meaning cleaning, or having soap-like properties)⁽⁵⁾.
- 3) **Cholesteric phase** (or chiral nematic)⁽⁶⁾.

3. Experimental

Materials and Techniques: All the chemicals (reagents and solvents) were supplied from Merck, BDH, Fluka and Alfa chemicals Co. and used as received. The infrared spectra of the prepared compounds were recorded using FT-IR 8300 Fourier transform infrared spectrophotometer of SHIMADZU Company as a potassium bromide (KBr) discs in the wave number range of (4000-400) cm⁻¹, in Al-Nahrain University, Iraq. Uncorrected melting points were recorded on hot stage Gallen kamp melting point apparatus. The ¹H-NMR spectra were recorded on Brüker ACF 300 spectrometer at 300 MHz, using deuterated chloroform or DMSO as solvent with TMS as an internal standard, in the

university of Exeter, England. Elemental analysis (CHNS-O) was carried out using EURO EA elemental analyzer instrument. Transition temperatures and enthalpies were scanned in TA instruments LINSEIS DSC PT-1000 differential scanning calorimeter with a heating rate of 10.0°C/min in air and it was calibrated with indium (156.6°C, 28.45 J/g). The temperatures were read as the maximum of the endothermic peaks. The optical behavior observations were made using MEIJI microscope equipped with INSTEC hot stage and central processor controller mK 1000 and connected with Lumenera color video camera, in Al-Nahrain University, Iraq.

Preparation of 4-n-Alkoxy benzoyl chlorides:

4-n-alkoxy benzoyl chlorides were prepared by reflux the corresponding *p*-n-alkoxy benzoic acid (0.02 mol) with freshly distilled thionyl chloride (10 mL) in water bath till evolution of hydrogen gas ceased. The excess thionyl chloride was distilled off under reduce pressure using water pump. The acid chloride left behind was directly used for further reaction without purification⁽⁷⁾.

Synthesis of 3,5-dialkoxybenzoic acid:

A mixture of 4-n-alkoxy benzoyl chloride (0.02mol) and 3,5-dihydroxy benzoic acid (0.01mol) with 10 mL pyridine were stirred for overnight in an ice bath. The mixture was poured onto cold water, acidification with HCl and filtered. The product was washed with cold water⁽⁸⁾.

Synthesis of 3,5-dialkoxybenzoyl chloride:

3,5-dialkoxybenzoyl chloride were prepared by reflux the corresponding product 3,5-dialkoxybenzoic acid with freshly distilled thionyl chloride (10 mL) in water bath till evolution of hydrogen gas ceased. The excess thionyl chloride was distilled off under reduce pressure using water pump. The acid chloride left behind was directly used for further reaction without purification⁽⁷⁾.

Synthesis of *N,N'*-1,4-Phenylbis[3,5-dialkoxybenzamide]:

A mixture of 3,5-dialkoxybenzoyl chloride (0.01mol) and *P*-phenyldiamine (0.005mol) with 10 mL pyridine were stirred for overnight in an ice bath. The mixture was poured onto cold water, acidification with HCl and filtered. The product was washed with cold water⁽⁸⁾.

Table 1: Melting points and % yield of compounds (7a,b,d,e).

No.	Name of compound	Chemical formula	M.W. (g/mol)	Yield %	m.p °C
7a	N,N'-1,4-phenylBis[3,5-Di(<i>p</i> -propoxybenzoyl) benzamide]	C ₆₀ H ₅₆ N ₂ O ₁₄	1029.1	76	142-146
7b	N,N'-1,4-phenylBis[3,5-Di(<i>p</i> -butoxybenzoyl) benzamide]	C ₆₄ H ₆₄ N ₂ O ₁₄	1082.2	58	127-131
7d	N,N'-1,4-phenylBis[3,5-Di(<i>p</i> -heptyloxybenzoyl) benzamide]	C ₇₆ H ₈₈ N ₂ O ₁₄	1253.5	83	114-120
7e	N,N'-1,4-phenylBis[3,5-Di(<i>p</i> -octyloxybenzoyl) benzamide]	C ₈₀ H ₉₆ N ₂ O ₁₄	1309.6	75	108-112

Synthesis of N,N'-1,4-phenylbis[3,4,5-trihydroxybenzoic acid]:

Gallic acid (0.003mol, 0.56g), *P*-phenyldiamine (0.001mol, 0.1g) and a catalytic amount of *P*-toluensulfonic acid were dissolved in dioxane (5mL) in a distillation system. The mixture was heated at 160 °C for 5 hour. The reaction mixture was allowed to reach room temperature and then was cooled by a water-ice bath to give a precipitate that was filtered and washed with gently quantities of diethyl ether⁽⁹⁾.

Synthesis of N,N'-1,4-phenylbis[3,4,5-Tri(*p*-alkoxybenzoyl) benzamide]:

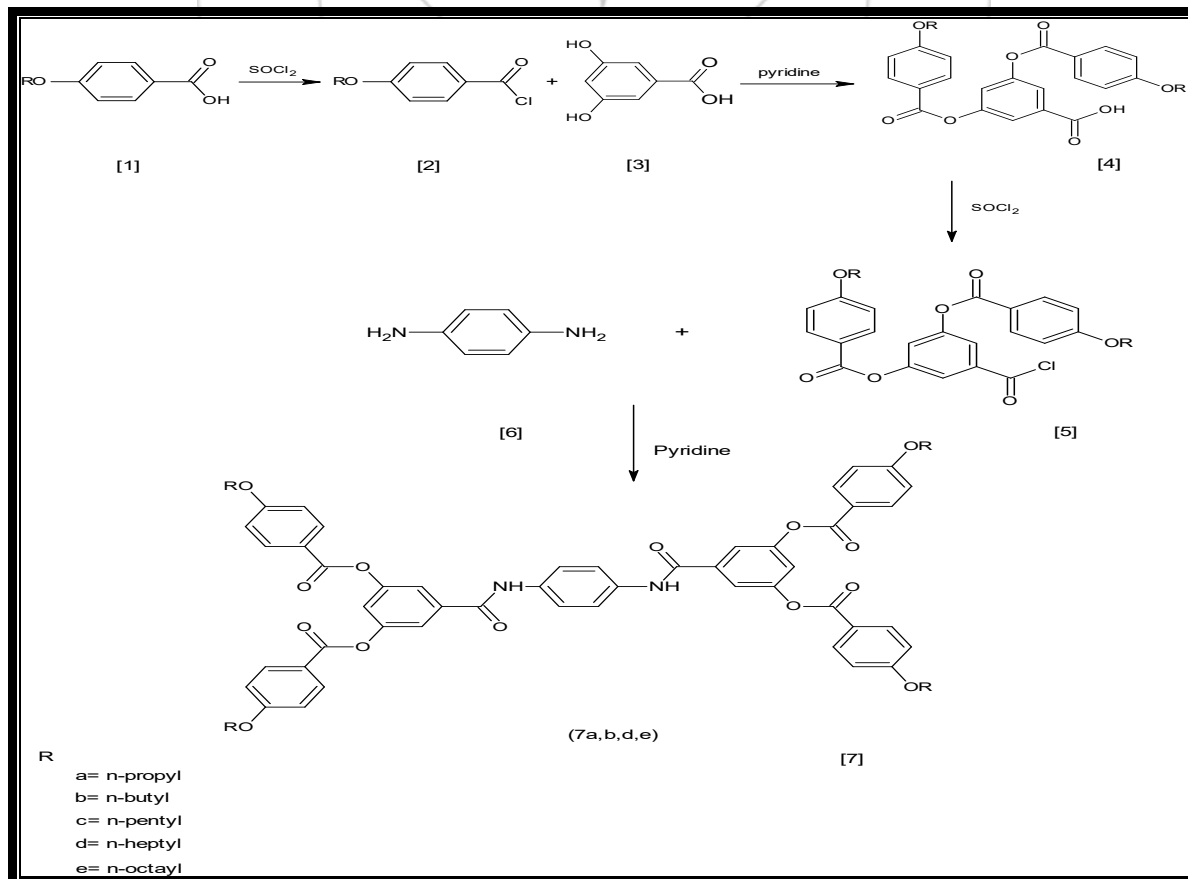
A mixture of *P*-alkoxybenzoyl chloride (0.018mol) and N,N'-1,4-phenylbis[3,4,5-trihydroxybenzoic acid] (0.003mol) with 10 mL pyridine were stirred for overnight in an ice bath. The mixture was poured onto cold water, acidification with HCl and filtered. The product was washed with cold water⁽⁸⁾.

Table 2: Melting points and % yield of compounds (10a-e)

No.	Name of compound	Chemical Formula	M.W. (g/mol)	Yield %	m.p °C
10a	N,N'-1,4-phenylbis[3,4,5-Tri(<i>p</i> -propoxybenzoyl) benzamide]	C ₈₀ H ₇₆ N ₂ O ₂₀	1385.40	75	156-161
10b	N,N'-1,4-phenylbis[3,4,5-Tri(<i>p</i> -butoxybenzoyl) benzamide]	C ₈₆ H ₈₈ N ₂ O ₂₀	1469.7	63	171-179
10c	N,N'-1,4-phenylbis[3,4,5-Tri(<i>p</i> -pentyloxybenzoyl) benzamide]	C ₉₂ H ₁₀₀ N ₂ O ₂₀	1553.77	60	136-141
10d	N,N'-1,4-phenylbis[3,4,5-Tri(<i>p</i> -heptyloxybenzoyl) benzamide]	C ₁₀₄ H ₁₂₄ N ₂ O ₂₀	1722.1	65	128-132
10e	N,N'-1,4-phenylbis[3,4,5-Tri(<i>p</i> -octyloxybenzoyl) benzamide]	C ₁₁₀ H ₁₃₆ N ₂ O ₂₀	1806.26	78	119-121

4. Results and Discussion

The steps of the synthesis of N,N'-1,4-phenylbis[3,5-Di(*p*-alkoxybenzoyl) benzamide] are shown in the sequence of reactions depicted in Scheme (1):



Scheme (1): The synthetic pathway for N,N'-1,4-phenylbis[3,5-Di(*p*-alkoxybenzoyl) benzamide] [7a,b,d,e]

The reaction of 3,5-di[4'-alkoxybenzoyloxy]benzoylchloride (5) with 1,4-phenylene diamine involve nucleophilic substitution reaction through tetrahedral mechanism.

The synthesis of compounds (7_{a-e}) was outlined in scheme (1). The synthesized compounds were identified by FT.IR, ¹H-NMR and elemental analysis (CHNS). The FT.IR spectra show the disappearance of two absorption band due to (-NH₂) str. of amine with appearance band at (1665-1685) cm⁻¹ due to amide (I) (C=O)[10]. Moreover, all compounds exhibit significant stretching bands near the region (3400, 2920, 1728, 1676, 1600, 1260) cm⁻¹, these indicated the presence of (N-H, C-H, C=O (ester), C=O (amide) C=C, C-O) groups [11]. Table (2) shows the characteristic FTIR absorption bands for compounds (7_{a-e}), while table (3) shows the (CHNS) value for the synthesized compounds. ¹H-NMR spectrum of compound (7d), showed the following characteristics chemical shifts (DMSO as a solvent): δ 6.2-

7.8 m, (aromatic); δ 9.6 b (-NH); δ 0.96 t (-CH₃); δ 1.75 m (-CH₂-CH₂); δ 3.94 t (-CH₂).

Table 2: Characteristic FTIR absorption bands (cm⁻¹) of synthesized compounds [7_{a-e}]

Comp. No.	ν C-H Aliphatic	ν C=O Amide	ν C=C aromatic	ν C-O	ν N-H Amide
7a	2866	1675	1571	1286	3132
7b	2850	1682	1573	1272	3188
7d	2886	1673	1606	1190	3205
7e	2923	1685	1605	1220	3267

Table 3: Elemental Analysis (CHN) for compounds [7_{a,e}]

Comp. No	Formula	%C		%H		%N	
		Calc.	Found	Calc.	Found	Calc.	Found
7a	C ₆₀ H ₅₆ N ₂ O ₁₄	69.96	70.03	5.44	4.99	2.72	2.74
7e	C ₈₀ H ₉₆ N ₂ O ₁₄	73.30	74.04	7.33	7.08	2.13	2.96

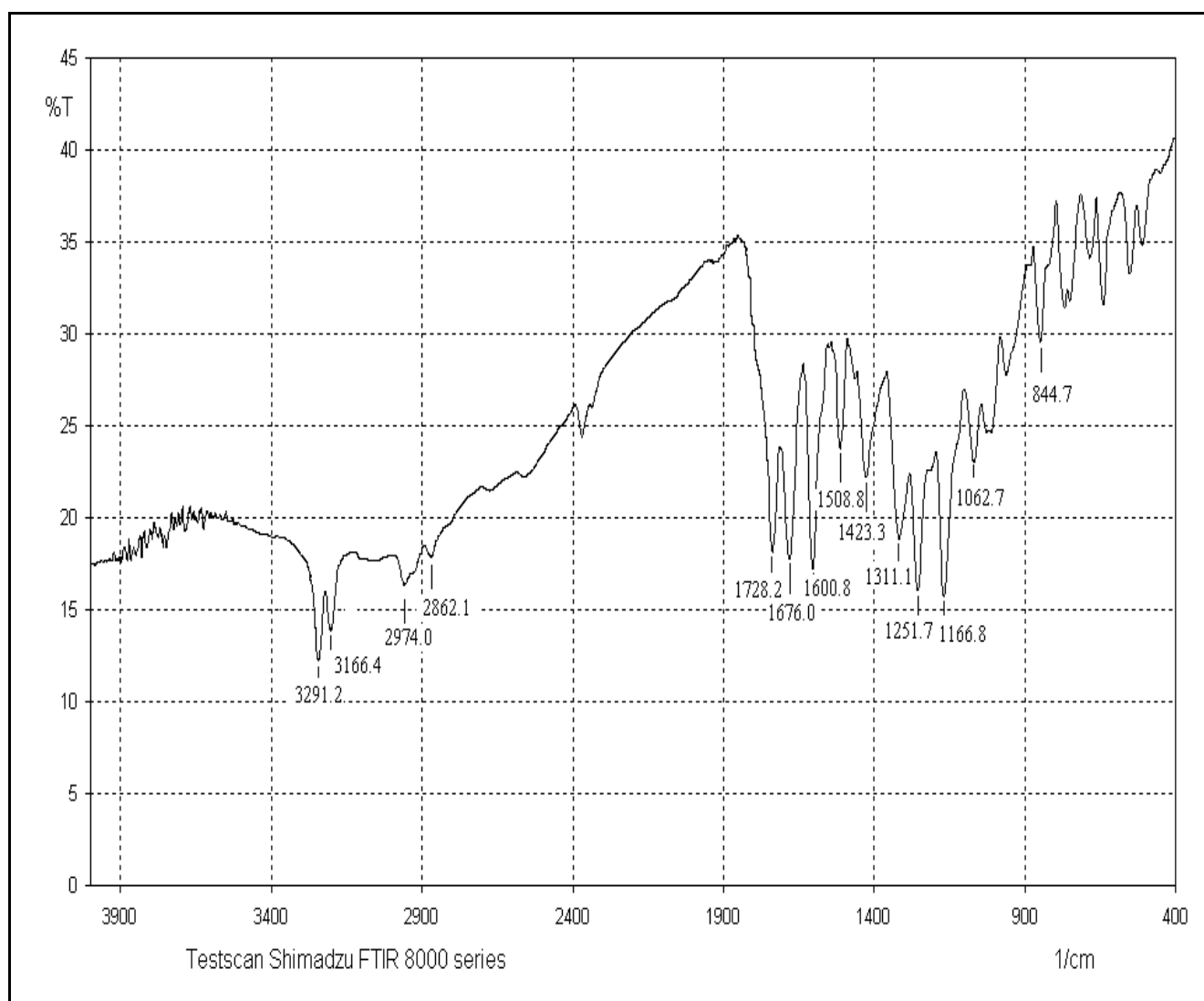


Figure 1: FTIR spectrum of N,N'-1,4-phenylbis[3,5-Di(p-butoxybenzoyl) benzamide]7b.

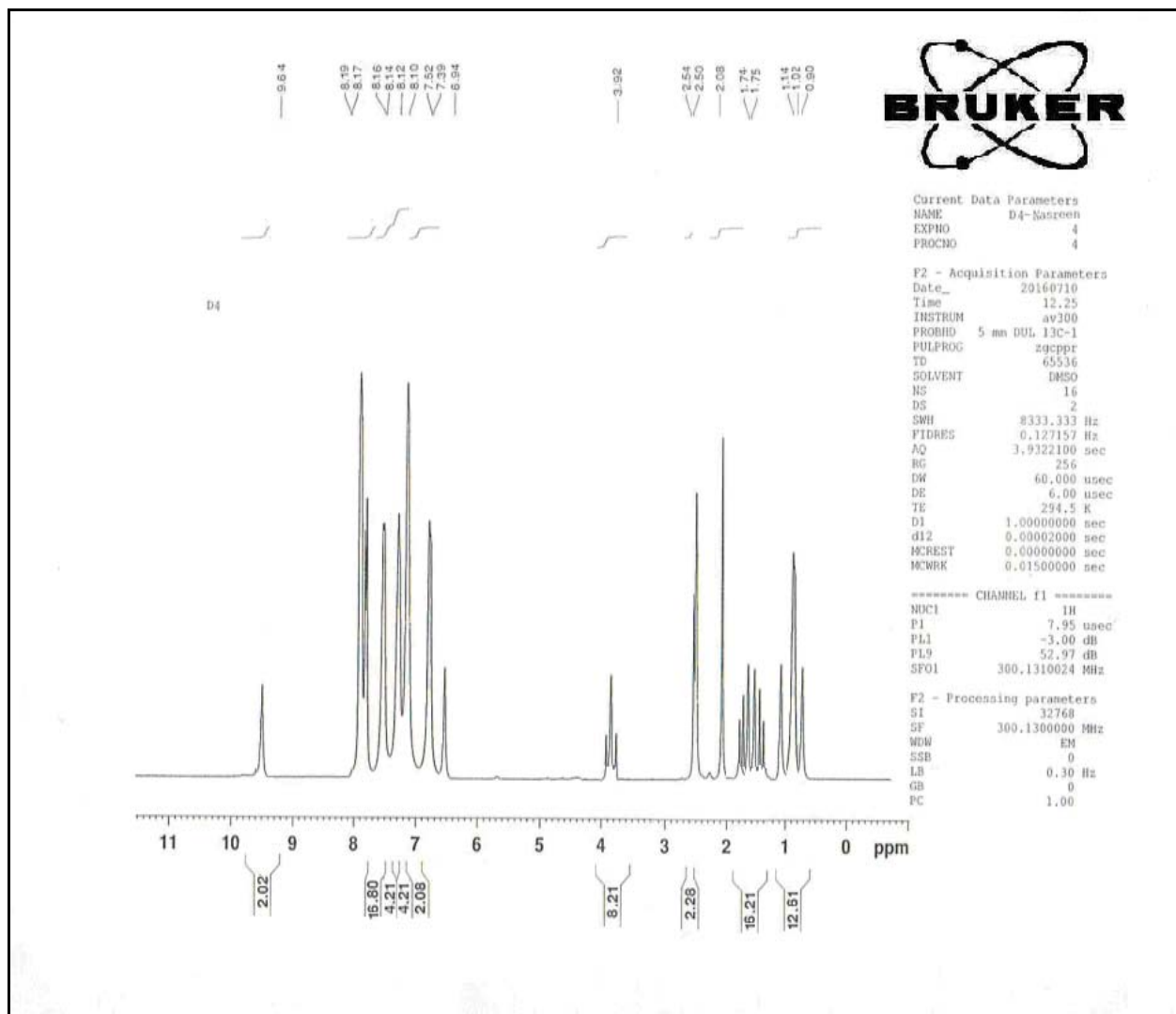
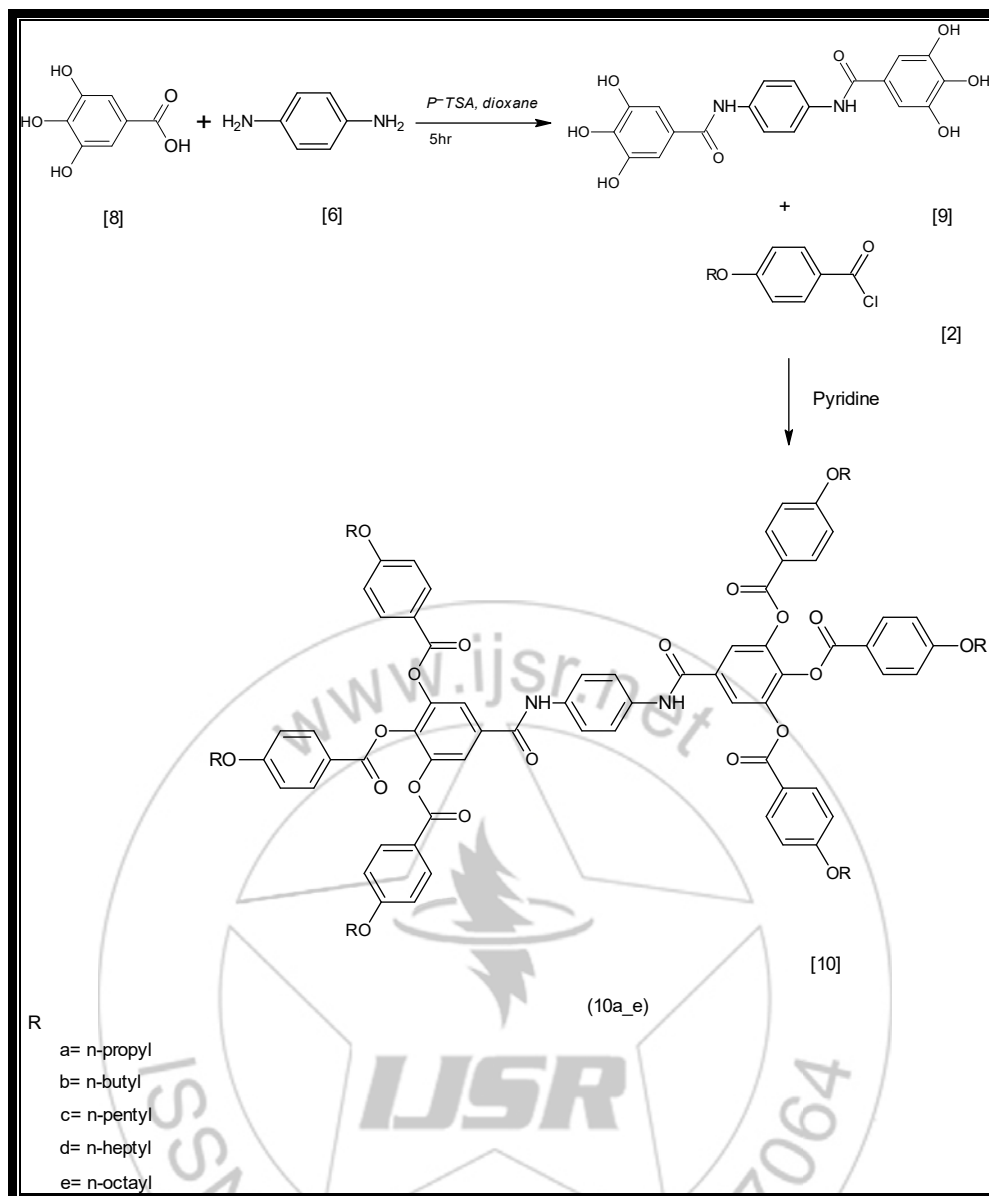


Figure 2: ¹H NMR spectrum of N,N'-1,4-phenylbis[3,5-Di(p-butyloxybenzoyl) benzamide] 7b.

The steps of the synthesis of N,N'-1,4-phenylbis[3,4,5-tri(p-alkoxybenzoyl) benzamide] are shown in the sequence of reactions depicted in Scheme 2.



Scheme (2): The synthetic pathway for N,N'-1,4-phenylbis[3,4,5-tri(p-alkoxybenzoyl) benzamide] [10a-e]

The titled compounds (10a-e) were synthesized through the reaction of N,N'-1,4-phenylbis[3,4,5-tri(*p*-hydroxy) benzene with three equivalents of the appropriate 4-alkoxybenzoyl chloride in dry pyridine. Table (4) show the elemental analysis of compounds [10a-e]. The structures of the synthesized compounds were identified by FT-IR, ¹H-NMR and elemental analysis (CHNS). The FT-IR spectra show the disappearance of two absorption band due to (-NH₂) str. of amine with appearance band at (1685-1700) cm⁻¹ due to amide (I) (C=O)[10]. Moreover, all compounds exhibit significant stretching bands near the region (3300, 2950, 1730, 1685, 1600, 1250) cm⁻¹, these indicated the presence of (N-H, C-H, C=O (ester), C=O (amide) C=C, C-O) groups [11]. Table (5) shows the characteristic FTIR absorption bands for compounds (10a-e). ¹H-NMR spectrum of compound (10b), showed the following characteristics chemical shifts (DMSO as a solvent): δ 7.2-7.9 m,

(aromatic); δ 9.5 s (-NH); δ 4.99-5.03 t (CH₂-CH₂) δ 0.99 t (-CH₃); δ 1.99 m (-CH₂).

Table 4: The Elemental Analysis (CHN) for compounds [10a-e]

Comp. No	Formula	%C		%H		%N	
		Calc.	Found	Calc.	Found	Calc.	Found
10b	C ₈₆ H ₈₈ N ₂ O ₂₀	70.22	69.71	5.98	5.61	1.90	2.02

Table 5: Characteristic FTIR absorption bands (cm⁻¹) of synthesized compounds [10]

Comp. No.	ν C-H Aliphatic	ν C=O Amide	ν C=C aromatic	ν C-O	ν N-H Amide
10a	2886	1669	1602	1259	3206
10b	2841	1678	1600	1245	3398
10c	2871	1679	1602	1255	3326
10d	2966	1680	1618	1220	3340
10e	2923	1692	1616	1259	3215

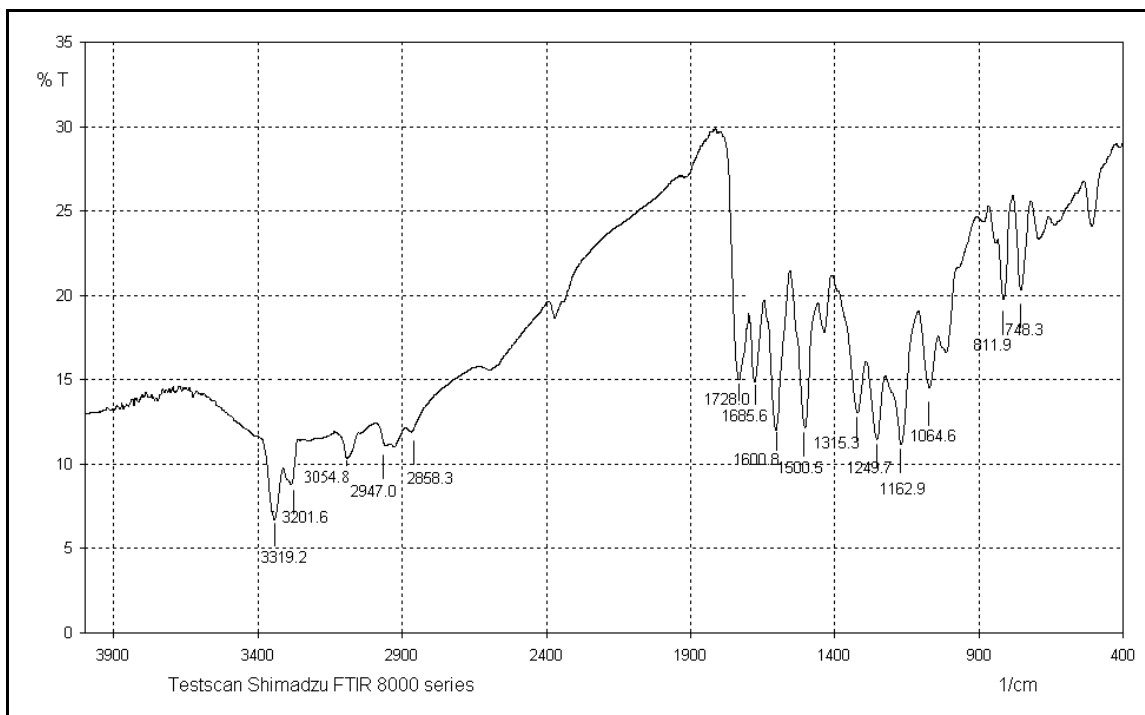


Figure 3: FTIR spectrum of N,N'-1,4-phenylbis[3,4,5-tri(p-pentoxybenzoyl) benzamide]10e.

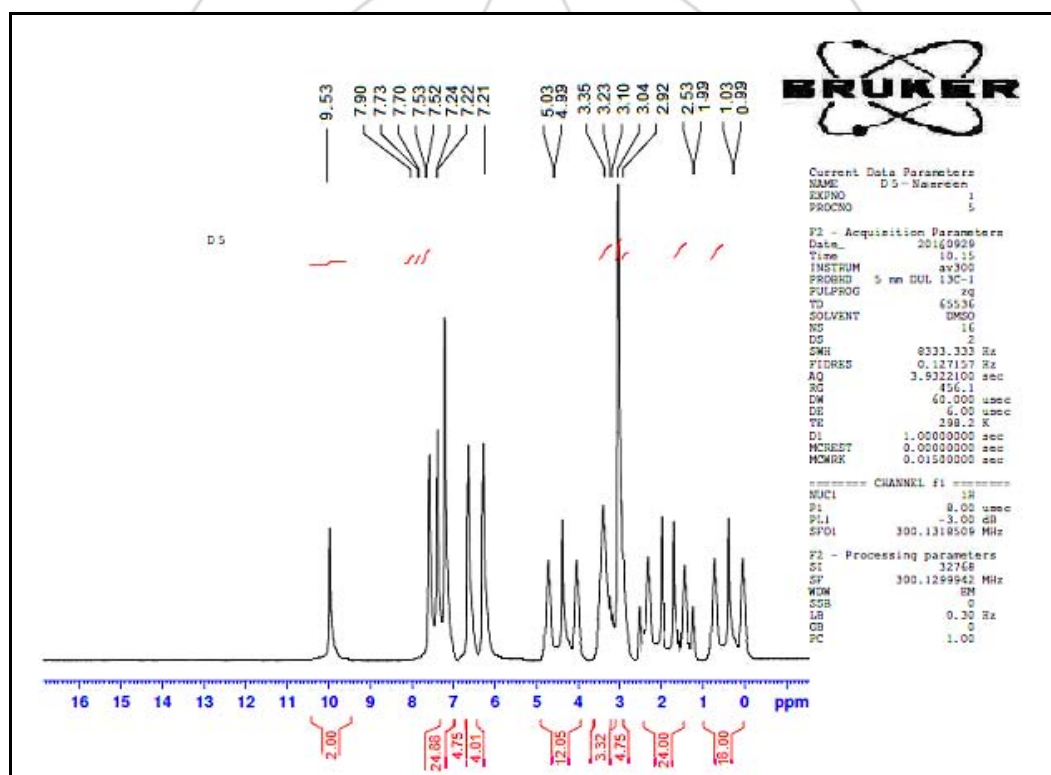


Figure 4: ¹H NMR spectrum of N,N'-1,4-phenylbis[3,4,5-tri(p-butyloxybenzoyl) benzamide]10b.

Mesomorphic Properties

Liquid crystalline properties of compounds 7a-e were examined by means of differential scanning calorimeter (DSC) and hot stage polarizing microscope. Compounds 7d and 7e showed a nematic mesophase of a typical thread-like texture as shown in Figure 5. The DSC thermogram of

compound 7 e is shown in Figure 6, which shows two transitions, the temperature at the maximum of the first transition peaks was chosen as the actual transition temperature, Crystal to Nematic (C → N), at 127°C, and the second one is the transition from Nematic to Isotropic (N → I) at 172 °C.

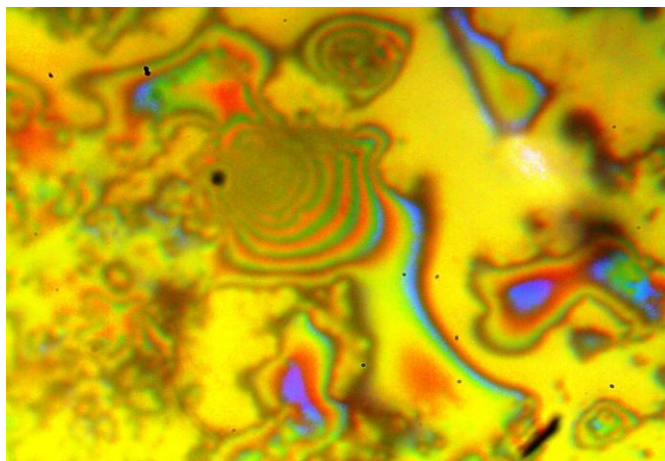


Figure 5: Schlieren texture of the nematic phase of compound 7e at 133°C (magnification 10× 10).

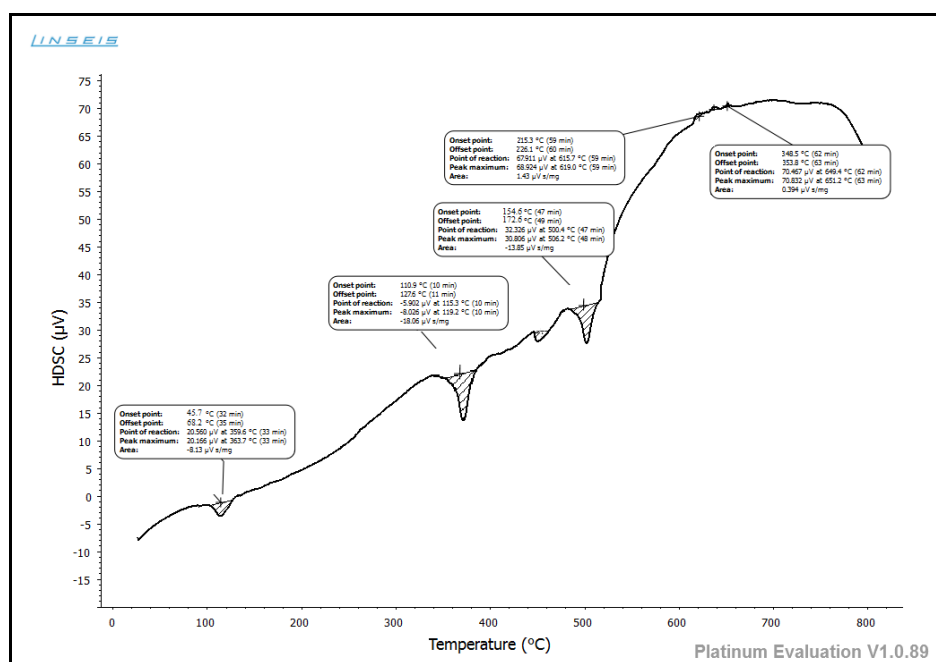


Figure 6: Differential scanning thermogram of compound 7e as a function of temperature for the second heating and cooling cycles (at scan rate 10 °C min⁻¹)

References

- [1] Lu Guang Chen, Thermo-Optical Properties of Polymer Dispersed Liquid Crystals, Science, Engineering and Technology Portfolio RMIT University, 2007.
- [2] Prajakta P. Gaikwad, Maya T. Desai, Liquid Crystalline Phase & its Pharma Applications, International Journal of Pharma Research & Review, 2(12), 2013.
- [3] T. Y. Puttewar, A. A. Shinde and R. Y. Patil, A REVIEW ON LIQUID CRYSTALS - A NOVEL DRUG DELIVERY SYSTEM, Shankarrao Ursal College of Pharmaceutical Sciences and Research Centre, Vol 4, 2014.
- [4] J. A. Regoa, J.A. Harveyb, A. L. MacKinnonb & E. Gatdulaa, "Asymmetric synthesis of a highly soluble 'trimeric' analogue of the chiral nematic liquid crystal twistagent Merck S1011", Liquid Crystals, vol 37, 37-43, 2010.
- [5] M. Sahara, S. Yano, K. Ikemoto and Z. Maejima, *Liq. Cryst.*, 15, 929-931, 1993.
- [6] YING ZHOU, CHOLESTERIC LIQUID CRYSTAL PHOTONIC CRYSTALLASERS AND PHOTONIC DEVICES, A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Optics and Photonics at University of Central Florida Orlando, Florida, 2008.
- [7] Chauhan M., and A. Doshi, "Study of an azoester novel homologous series: 4-[4'-n-alkoxy benzoyloxy]-3-methoxy phenyl azo- 3"- chloro benzenes ", *Pharma Chemica*, 3(1), 172-180 (2012).
- [8] Chauhan, D. K. Bhoi, M. T. Machhar, D. K. Solanki and Dhaval Solanki, "Synthesis, characterization and mesomorphic properties of azoester mesogens: 4-n-alkoxybenzoic acid 4-[3-(benzylidene-amino)-phenylazo]-phenyl ester ", *Pharma Chemica*, 2(4), 30-37, (2010).
- [9] Rivero-Buceta E, Carrero, "Linear and branched alkyl-esters and amides of gallic acid and other (mono-, di- and tri-) hydroxy benzoyl derivatives as promising anti-HCV inhibitors" *Eur J Med Chem.*, 2015.