



Bis-Swallow-Tailed Alkoxy-Substituted Di and Tri hydroxyl benzoic acid: Synthesis, Photophysical Properties and Thermotropic Behaviors

*Donya M. Hadi, Nasreen R. Jber

*Department of Chemistry, College of Sciences, Al-Nahrain University, Baghdad-Iraq.

Abstract : A new series of bis-swallow-tailed mesogens N,N'-1,4-biphenyl-lbis[3,5-Di(4'-alkyloxybenzoylox) benzamide] and N,N'-1,4-biphenyl-bis[3,4,5-Tri(4'-alkyloxybenzoylox) benzamide] are synthesized. The synthesized compounds were characterized using FT-IR, CHNS analysis and ¹H-NMR. The liquid crystalline properties of the prepared compounds, the effect of these ends on the mesogenic properties and their Transitional stability were verified using hot-stage polarizing optical microscope (POM) differential scanning calorimeter (DSC).

Keywords : Liquid crystalline, Mesogen, Mesomorphism.

Introduction:

Liquid crystals are mesophases between crystalline solids and isotropic liquid⁽¹⁾. Mesogen (or LC) is a compound that shows liquid crystal properties which is composed of molecules each with an elongated rigid core with, at one end, a branched flexible chain, having branches of about the same length⁽²⁾. Terminal and lateral substituents and geometrical shape of a molecule play an important role in mesomorphic properties of a mesogen⁽³⁾. The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules (mesogens) to point along a common axis, called the director. This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term "mesogenic state" used synonymously with liquid crystal state. Polymorphism arises between the transformation of crystal to isotropic fluid due to weak intermolecular forces that imparts the equilibrium, results in well-defined phase changes. This was known as mesomorphism and the phases known as 'mesophases'⁽⁴⁾. LCs are anisotropic materials whose flow properties strongly depend on their structures and molecular orientation⁽⁵⁾.

Experimental:

Materials and Techniques:

All the chemicals (reagents and solvents) were supplied from Merck, BDH, Fluka and Alfa chemicals Co. and used as received.

Preparation of *P*-alkyloxy benzoic acids:

P-Hydroxy benzoic acid (1.38 g, 0.1 mol), alkyl halides (0.12 mol) and KOH (0.25 mol) were dissolved in (10 mL) methanol and reaction mixture was refluxed about 4 hour. 10% aqueous KOH solution (20 mL) was

added and refluxing continued for further two hours. The solution was cooled and acidified with HCl to precipitate⁽⁶⁾.

Preparation of *P*-alkoxybenzoylchloride:

4-*n*-alkoxy benzoyl chlorides were prepared by reflux the corresponding *p*-alkoxy benzoic acid (0.02mol) with thionyl chloride (10 mL) in water bath for 2 hr. The excess thionyl chloride was distilled off⁽⁷⁾.

Synthesis of 3,5-di(*p*-alkoxybenzoyl) benzoic acid:

A mixture of *P*-alkoxybenzoyl chloride (0.02mol) and 3,5-dihydroxybenzoic 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⁾.

Table (2.4) Physical properties of the compounds [16a-e].

No.	Name of compound	Chemical formula	M.W. (g/mol)	Yield %	m.p °C
16a	3,5-di[4-propoxybenzoyloxy]benzoic acid	C ₂₇ H ₂₆ O ₈	478.49	74	254-272
16b	3,5-di[4-butoxybenzoyloxy]benzoic acid	C ₂₉ H ₃₀ O ₈	506.54	68	263-281
16c	3,5-di[4-pentoxybenzoyloxy]benzoic acid	C ₃₁ H ₃₄ O ₈	534.59	77	203-218
16d	3,5-di[4-heptoxybenzoyloxy]benzoic acid	C ₃₅ H ₄₂ O ₈	590.70	70	189-205
16e	3,5-di[4-octoxybenzoyloxy]benzoic acid	C ₃₇ H ₄₆ O ₈	618.76	84	176-184

Synthesis of 3,5-di(*p*-alkoxybenzoyl) benzoylchloride:

3,5-di(*p*-alkoxybenzoyl) benzoylchloride were prepared by reflux the corresponding product 3,5-di(*p*-alkoxybenzoyloxy)benzoic acid with thionyl chloride (10 mL) in water bath for 3 hr. The excess thionyl chloride was distilled⁽⁷⁾.

Synthesis of N,N'-1,4-biphenyl-bis[3,5-Di(4'-alkoxybenzoylox) benzamide]:

A mixture of 3,5-di(*p*-alkoxybenzoyl) benzoylchloride (0.01mol) and benzidine (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 (2.5) Physical properties of the compounds [18a-e].

No.	Name of compound	Chemical formula	M.W. (g/mol)	Yield %	m.p °C
18a	N,N'-1,4-biphenyl-bis[3,5-Di(<i>p</i> -propoxybenzoyloxy)benzamide]	C ₆₆ H ₆₀ N ₂ O ₁₄	1105.2	64	261-279
18b	N,N'-1,4-biphenyl-bis[3,5-Di(<i>p</i> -butoxybenzoyloxy)benzamide]	C ₇₀ H ₆₈ N ₂ O ₁₄	1161.29	70	243-257
18c	N,N'-1,4-biphenyl-bis[3,5-Di(<i>p</i> -pentoxybenzoyloxy)benzamide]	C ₇₄ H ₇₆ N ₂ O ₁₄	1217.4	77	212-229
18d	N,N'-1,4-biphenyl-bis[3,5-Di(<i>p</i> -heptoxybenzoyloxy)benzamide]	C ₈₂ H ₉₂ N ₂ O ₁₄	1329.6	72	208-218
18e	N,N'-1,4-biphenyl-bis[3,5-Di(<i>p</i> -octyloxybenzoyloxy)benzamide]	C ₈₆ H ₁₀₀ N ₂ O ₁₄	1385.7	69	196-206

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

Gallic acid (0.003mol, 0.56g), benzidine (0.001mol) and a catalytic amount of *P*-toluensulfonic acid were dissolved in dioxane (5mL). The mixture was refluxed 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-biphenyl-bis[3,4,5-Tri(*p*-alkoxybenzoyl)benzamide] and:

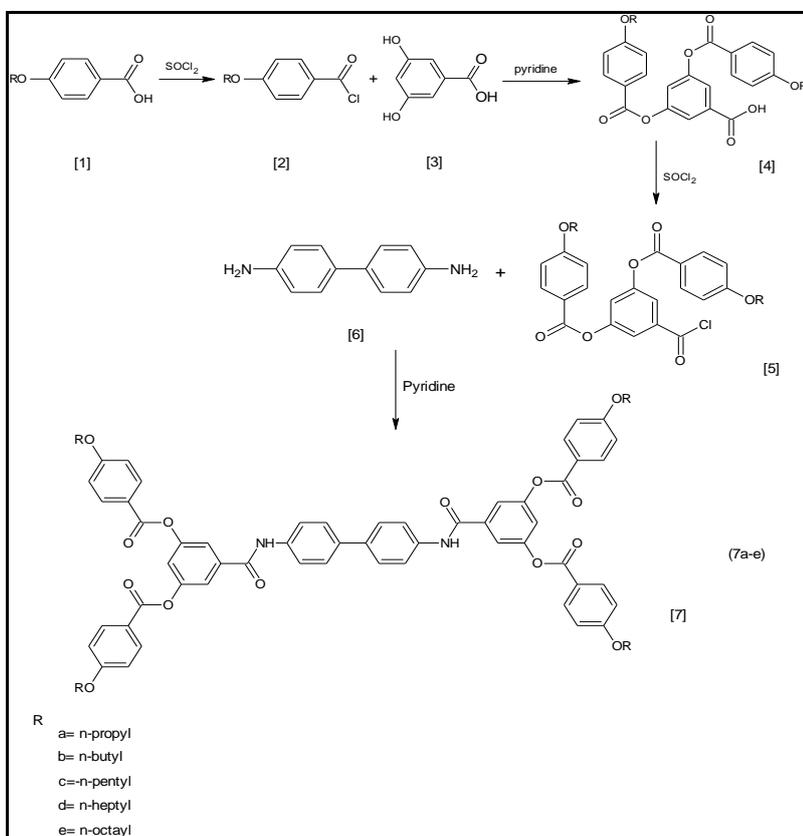
A mixture of *P*-alkoxybenzoyl chloride (0.018mol) and N,N'-1,4-biphenyl-bis[3,4,5-trihydroxybenzoic acid] (0.003mol) with 10 mL pyridine were stirred for overnight in an ice bath. The mixture was poured onto cold water, acidification with HCl and filtered. The product was washed with cold water⁽⁸⁾.

Table (2.7) Physical properties of the compounds [22a-e].

No.	Name of compound	Chemical Formula	M.W. (g/mol)	Yield %	m.p °C
22a	N,N'-1,4-biphenyl-bis[3,4,5-Tri(<i>p</i> -propoxybenzyloxy)benzamide]	C ₈₆ H ₈₀ N ₂ O ₂₀	1461.55	73	223-229
22b	N,N'-1,4-biphenyl-bis[3,4,5-Tri(<i>p</i> -butoxybenzyloxy)benzamide]	C ₉₂ H ₉₂ N ₂ O ₂₀	1545.7	60	215-218
22c	N,N'-1,4-biphenyl-bis[3,4,5-Tri(<i>p</i> -pentyloxybenzyloxy)benzamide]	C ₉₈ H ₁₀₄ N ₂ O ₂₀	1629.57	65	210-215
22d	N,N'-1,4-biphenyl-bis[3,4,5-Tri(<i>p</i> -heptoxybenzyloxy)benzamide]	C ₁₁₀ H ₁₂₈ N ₂ O ₂₀	1798.19	71	203-209
22e	N,N'-1,4-biphenyl-bis[3,4,5-Tri(<i>p</i> -octyloxybenzyloxy)benzamide]	C ₁₁₆ H ₁₄₀ N ₂ O ₂₀	1885.35	88	195-201

Results and Discussion:

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



Scheme(1): The synthetic pathway N,N'-1,4-biphenyl-bis[3,5-Di-(*p*-alkoxybenzoyl) benzamide] (7)a-e.

The benzylation of 3,5-dihydroxy benzoic acid with 4-alkoxybenzoylchloride afford the preparation of 3,5-di-(4'-alkoxybenzoyloxy)benzoic acid (4)a-e. according to tetrahedral mechanism. The synthesis of compounds (7)_{a-e} was outlined in scheme (1). The synthesized compounds were identified by FT.IR, ¹HNMR and elemental analysis (CHNS). The FTIR spectrum show the disappearance of two absorption band due to (-NH₂) str. of amine with appearance of N-H stretching band of amide group at 3230 cm⁻¹ and the appearance of bands at 3062, 2952, 2860, 1728, 1677, 1596, 1251 and 1164 due to Ar-H, C-H aliph., C=O (ester), C=O (amide), C=C, C-O-C (asymm. And symm.) respectively. Table (2) show the FTIR bands value for compounds (7)_{a-e}. While the value of elemental analysis show in table (3).

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=O Ester	ν C=C aromatic	ν C-O	ν N-H Amide
7a	2951 2860	1680	1738	1600	1254 1158	3287
7b	2932 2865	1702	1741	1602	1254	3231
7c	2952 2860	1677	1728	1596	1251 1164	3230
7d	2987 2877	1698	1739	1597	1247 1164	3214
18e	2955	1681	1739	1598	1225	3220

Table (3) Elemental Analysis (CHN) for compounds (7)_{a,c,d}.

Comp. No	Formula	%C		%H		%N	
		Calc.	Found	Calc.	Found	Calc.	Found
7a	C ₆₆ H ₆₀ N ₂ O ₁₄	71.73	72.03	5.43	5.48	2.53	2.48
7c	C ₇₄ H ₇₆ N ₂ O ₁₄	73.02	72.98	6.25	6.14	2.30	2.29
7d	C ₈₂ H ₉₂ N ₂ O ₁₄	74.09	74.21	6.92	6.88	2.10	2.09

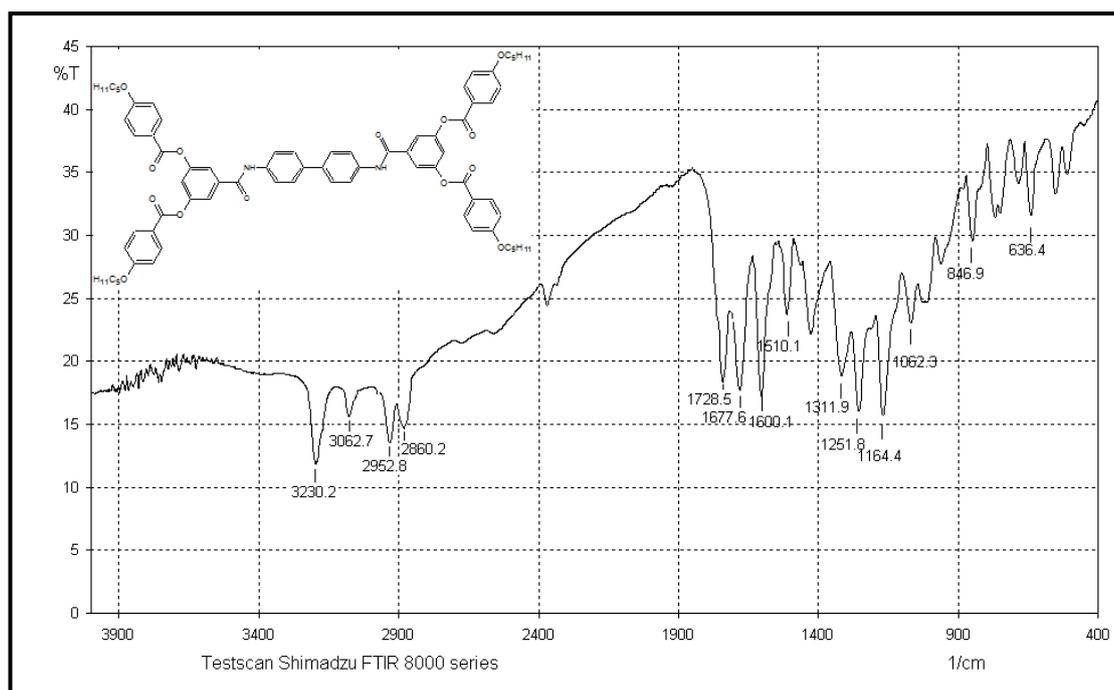


Figure (1): FTIR spectrum of N,N'-1,4-biphenyl-bis[3,5-di-(4'-pentoxybenzoyloxy)benzamide] (7)c.

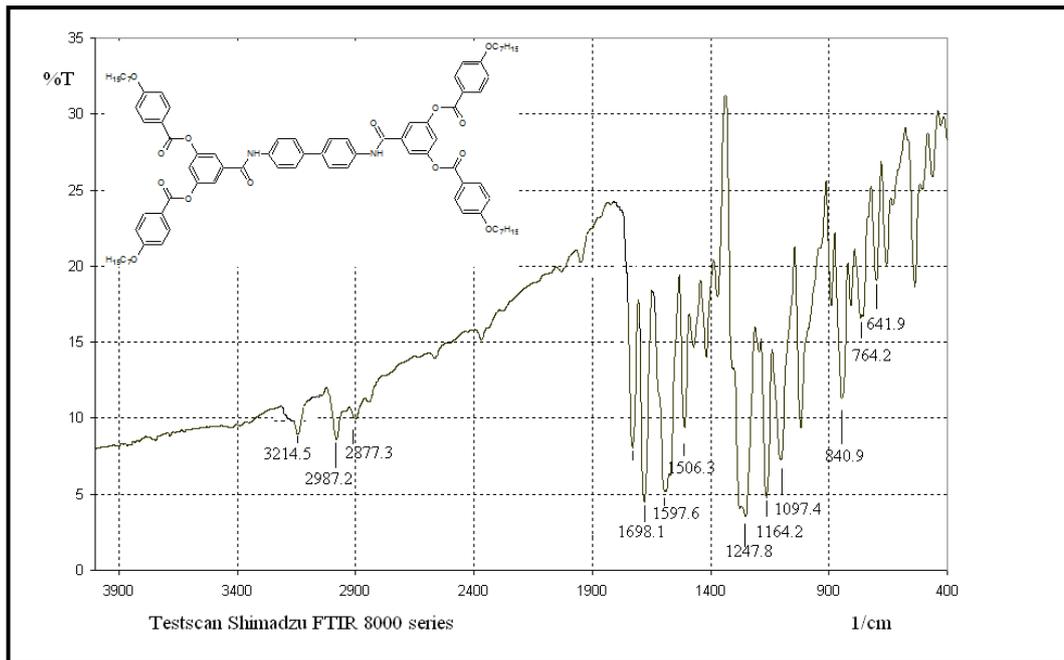
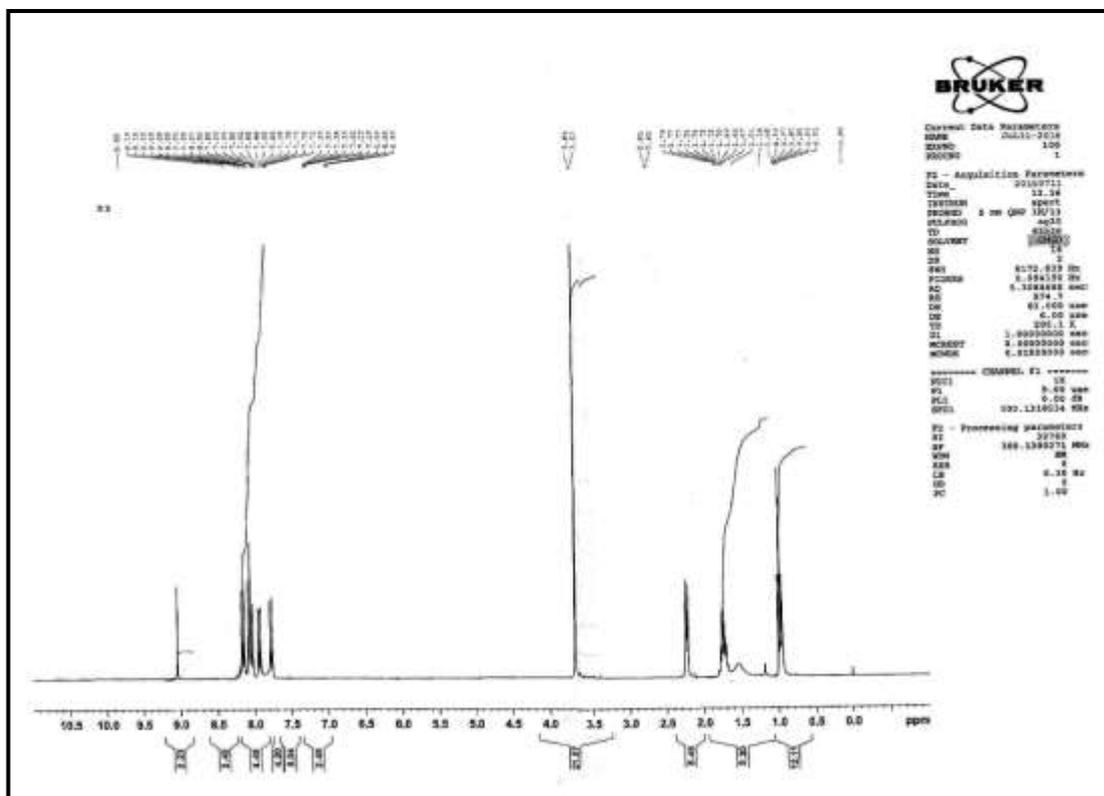


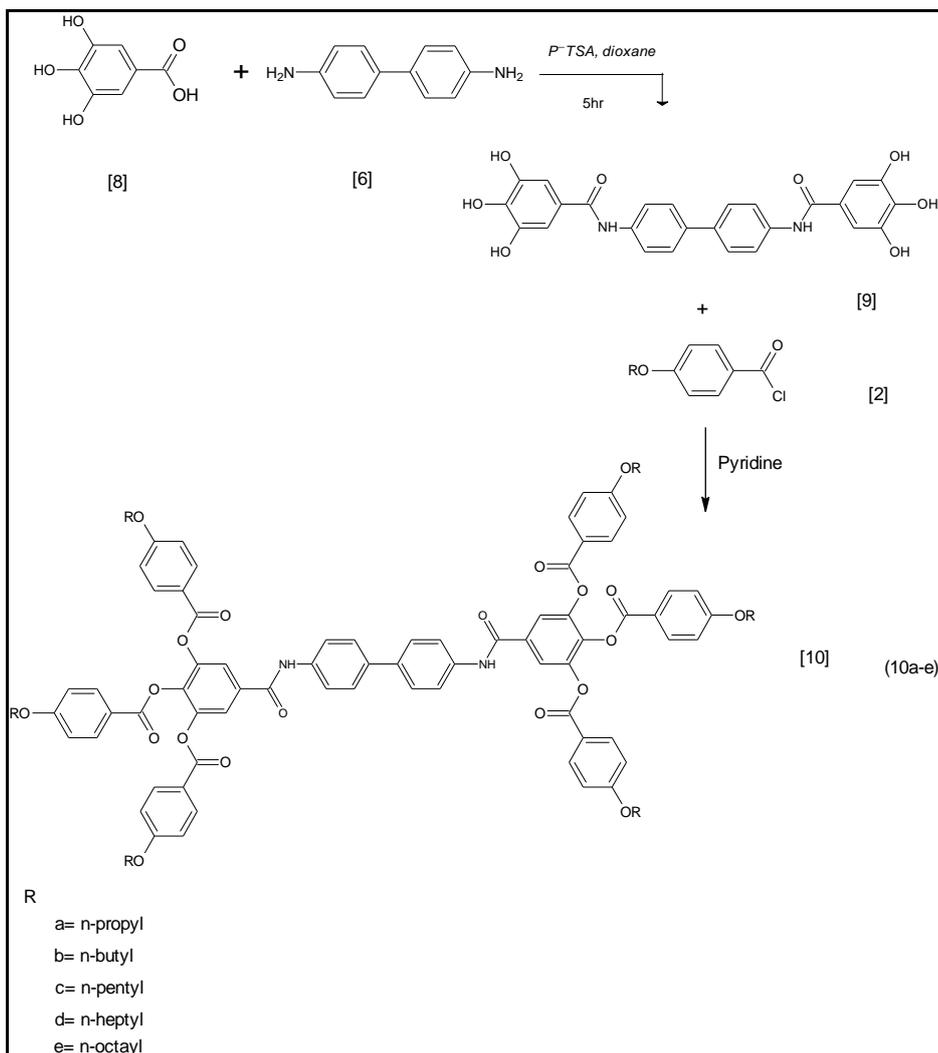
Figure (2):FTIR spectrum of N,N`-1,4-biphenyl-bis[3,5-di-(4`-heptoxybenzoyloxy)benzamide](7)d.

¹H-NMR spectrum of compound (7)a, showed the following characteristics chemical shifts (d₆-DMSO as a solvent, ppm): δ 6.93-8.15 m(aromatic);δ 9.06 b (-NH); δ0.93 – 1.18 t (-CH₃);δ 2.82 – 2.95(- CH₂);δ 1.54 – 1.79 t (- CH₂).



Figure(3):¹HNMR spectrum of N,N`-1,4-biphenyl-bis[3,5-di-(4`-propylbenzoyloxy)benzamide](7)a.

The steps of the synthesis of N,N'-1,4-biphenyl-bis[3,4,5-tri(*p*-alkoxybenzoyl) benzamide]are shown in Scheme (2):



Scheme (2): The synthetic pathway N,N'-1,4-biphenyl-bis[3,4,5-tri-(4'-alkoxybenzoyloxy) benzamide] (10).

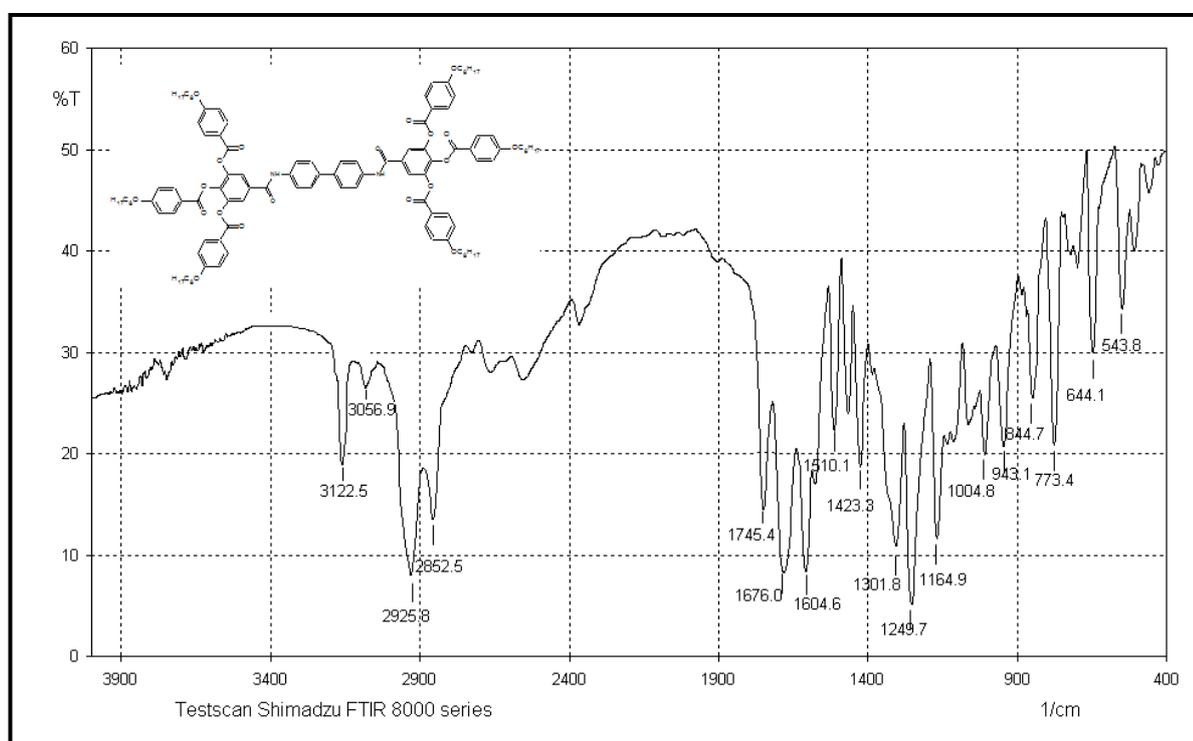
The synthetic steps involve the preparation of N,N'-1,4-biphenyl-bis[3,4,5-tri-(hydroxy)benzamide] by the reaction of gallic acid with benzidine, using *p*-toluenesulphonic acid as catalyst and dioxane as solvent⁽¹⁰⁾. The reaction of compounds (9) with 4-alkoxybenzoyl chloride affords the synthesis of N,N'-1,4-biphenyl-bis[3,4,5-tri-(4'-alkoxybenzoyloxy) benzamide] (10)a-e. The structures of the synthesized compounds were identified by FT-IR, ¹HNMR and elemental analysis (CHNS). The FT-IR spectrum of compound (10)e shows the disappearance of hydroxyl group stretching with the appearance of bands at 3122, 3056, 2925, 2852, 1745, 1676, 1604, 1249 and 1164 cm⁻¹ due to (N-H, C-H (aromatic), C-H (aliphatic), C=O (ester), C=O (amide), C=C, C-O-C) groups. Tables (4) and (5) show the characteristic FTIR absorption bands and elemental analysis for compounds (10) a-e respectively.

Table (4) The Elemental Analysis (CHN) for compounds (10)a,b.

Comp. No	Formula	%C		%H		%N	
		Calc.	Found	Calc.	Found	Calc.	Found
10a	C ₈₆ H ₈₂ N ₂ O ₂₀	70.58	71.03	5.60	5.87	1.91	2.02
10b	C ₉₂ H ₉₄ N ₂ O ₂₀	71.41	69.98	6.080	5.91	1.81	1.79

Table (5) Characteristic FTIR absorption bands (cm⁻¹) of synthesized compounds (10)a-e.

Comp. No.	ν C-H Aliphatic	ν C=O Amide	ν C=O Ester	ν C=C aromatic	ν C - O	ν N -H Amide
10a	2934,2866	1685	1746	1591	1286 1172	3324
10b	2953, 2869	1704	1732	1602	1253 1168	3288
10c	2931, 2828	1703	1732	1598	1246 1136	3231
10d	2921, 2831	1677	1742	1589	1294 1166	3287
10e	2925, 2852	1676	1745	1604	1249 1164	3122

**Figure (3): FTIR spectrum of N,N'-1,4-biphenyl-bis[3,4,5-tri(4'-octybenzoyloxy)benzamide](10)e.**

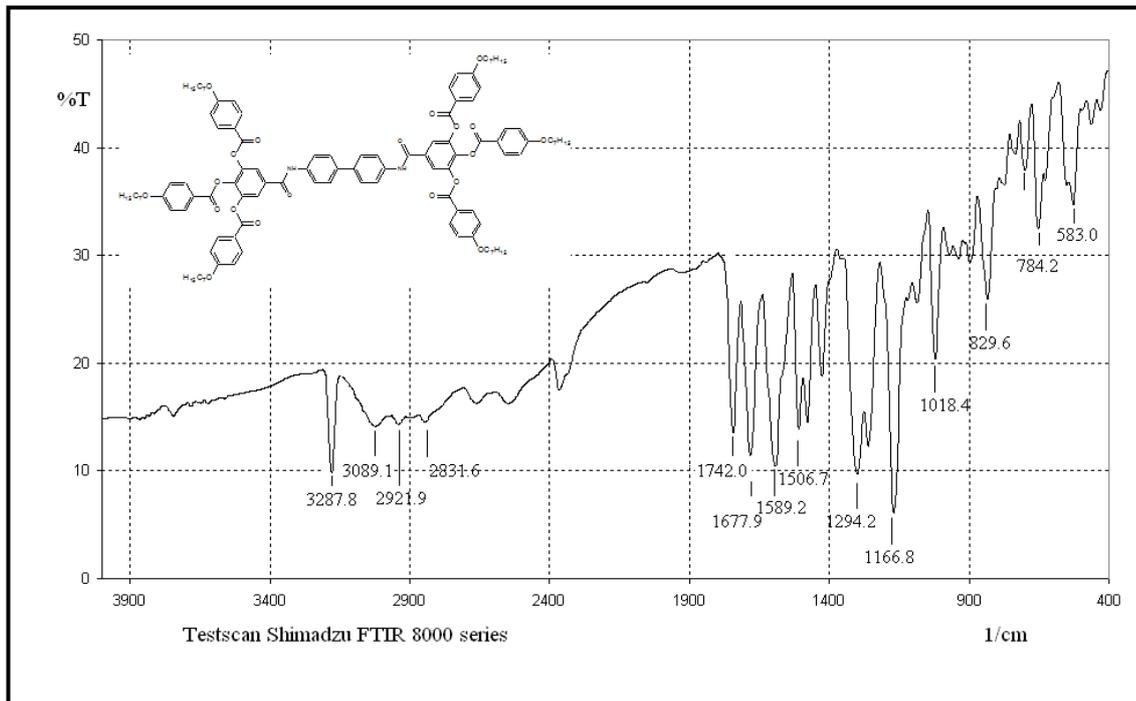


Figure (4): FTIR spectrum of N,N'-1,4-biphenyl-bis[3,4,5-tri(p-heptoxybenzoyloxy) benzamide](10)d.

¹H-NMR spectrum of compound (10)a, showed the following characteristics chemical shifts (d₆-DMSO as a solvent, ppm): δ6.6-8.1m (aromatic); δ 9.12b(-NH); δ0.9 – 1.0t(-CH₃); δ 2.8 – 2.9(-CH₂); δ 1.6 – 1.7t(-CH₂).

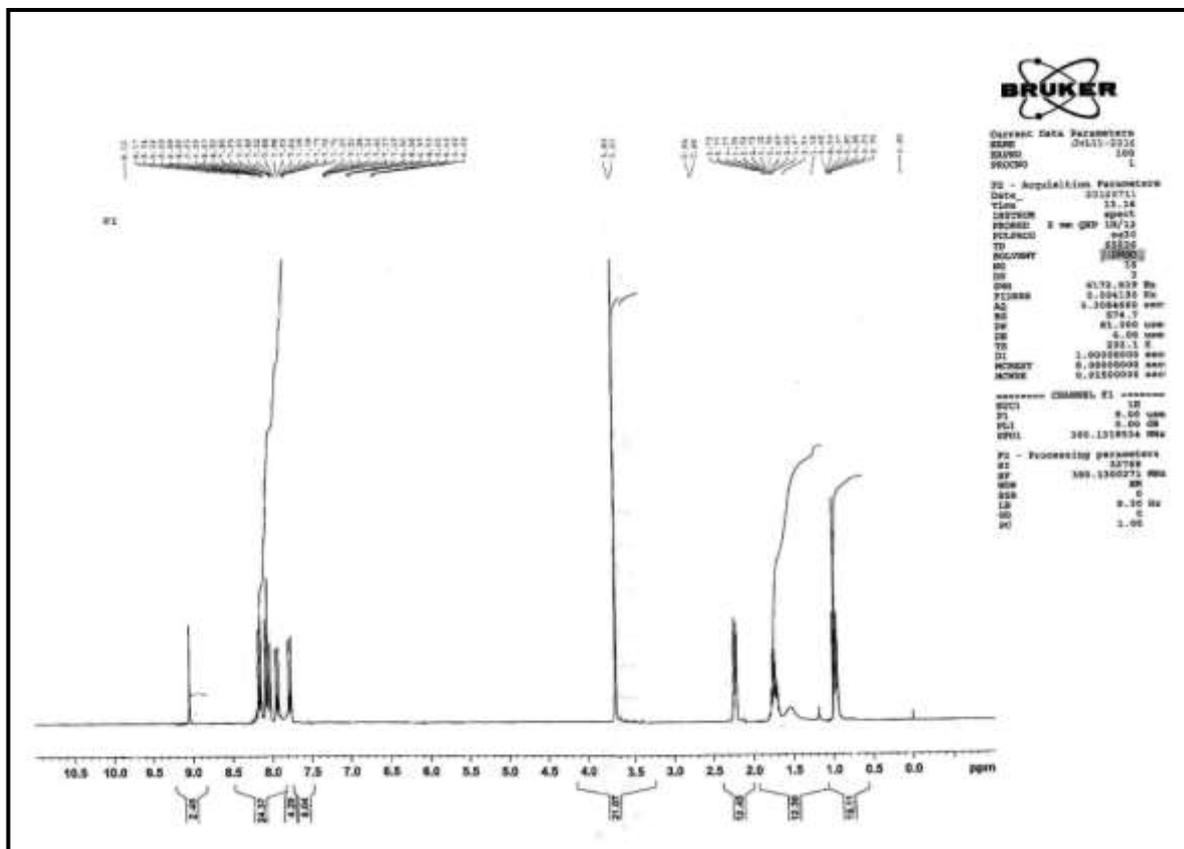


Figure (5): ¹H-NMR spectrum of N,N'-1,4-biphenyl-bis[3,4,5-tri(4'-propoxybenzoyloxy)benzamide](10)a.

Thermotropic Liquid Crystalline Properties of synthesized compounds

Bis swallow compound containing rigid core (biphenyl) have been regarded as the most suitable structure to obtain mesogenic properties⁽¹¹⁾. Most of known thermotropic liquid crystals are calamitic structurally⁽¹²⁾. A calamitic mesogen molecule consists of a core (e.g. aromatic rings), terminal chains (e.g. alkoxy group) and lateral substituents.

Phase Transitions

The phase transition temperatures were determined using differential scanning calorimetry (DSC). The DSC thermograms of compounds (7)a-e are shown in figure (6). Two exothermic peaks were found on cooling from the isotropic liquid. On heating to the isotropic liquid, a sharp melting peak appeared as shown in table (6). All the synthesized compounds show nematic mesophases.

Table (6) Melting points and type of transition for compounds (7)a-e.

Comp. No.	Melting point °C	Transition
7a	261-279	C → N
7b	243-257	C → N
7c	212-229	C → N
7d	208-218	C → N
7e	196-206	C → N

C = Crystal; N = Nematic.

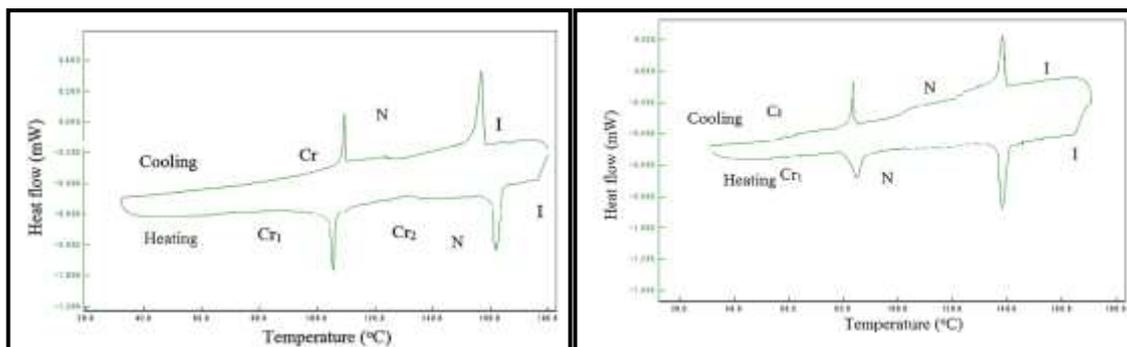


Figure (6): Differential scanning thermogram of compound 7a and 7d as a function of temperature for the second heating and cooling cycles (at scan rate 10 °C min⁻¹).

Compounds (10)a-e also examined by DSC as shown in figures (7) 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) and the second one is the transition from Nematic to Isotropic (N → I), as shown in table (7).

Table (7) Melting points and type of transition for compounds (10)a-e.

Comp. No.	Melting point °C	Transition
10a	223-229	C → N
10b	215-218	C → N
10c	210-215	C → N
10d	203-209	C → N
10e	195-201	C → N

C = Crystal; N = Nematic

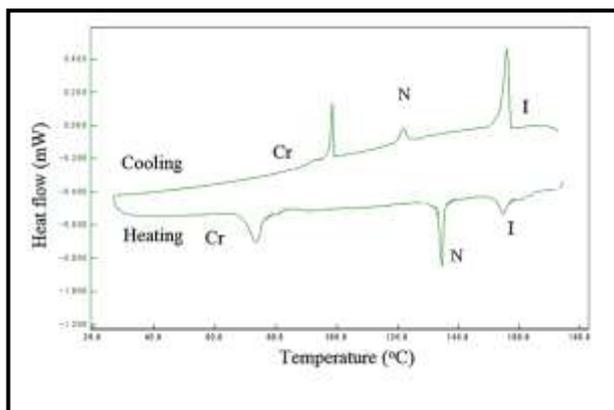


Figure (7): Differential scanning thermogram of compound 10d as a function of temperature for the second heating and cooling cycles (at scan rate $10\text{ }^{\circ}\text{C min}^{-1}$).

Phase structure:

The phase structures were determined by polarizing optical microscope (POM). The potential mesogenic properties of (7)a-e have been checked with a polarizing microscope equipped with a heating stage and a single melting point has been noticed at $196 - 261\text{ }^{\circ}\text{C}$. This behaviour may be explained by the flexibility of molecule ⁽¹²⁾.

The presence of a biphenyl ring into the principle structure of compound (7)a-e could cause considerable changes of polarity, polarizability and geometry of the molecules and influenced the type and the phase transition temperature of the mesophases ⁽¹⁴⁾. Liquid crystalline properties of compound (10)a-e also were examined by means of hot stage polarizing microscope which showed nematic mesophase, Figure (8).

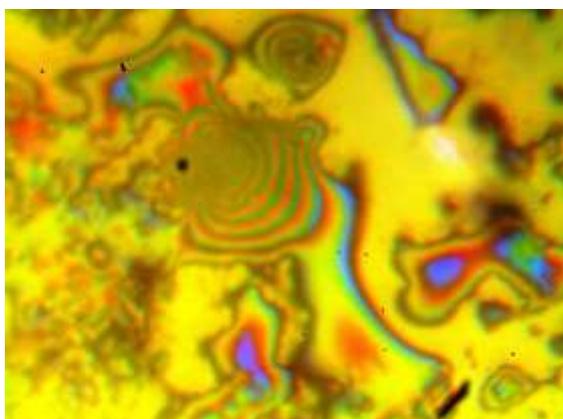


Figure (8): Schlieren texture of the nematic phase of compound 10d at 206°C (magnification 10×10).

References:

1. Den K. Yang and Shin T. Wu, Fundamentals of Liquid Crystal Devices, John Wiley & Sons Ltd, 1-2, 2006.
2. BARÓN AND R. F. T. STEPTO, DEFINITIONS OF BASIC TERMS RELATING TO POLYMER LIQUID CRYSTALS, INTERNATIONAL UNION FOR PURE AND APPLIED CHEMISTRY, Vol. 74, No. 3, pp. 493–509, 2002.
3. H. Kelker., "Handbook of liquid crystals", eds H. Kelker and R. Hatz., Wenham, Verlag Chemie, 1980.
4. Suzuki and N. Koide, Synthesis and Characterization of Biphenylethynylbenzene Type Discotic Liquid Crystal, vol.364,1,635-645, 2001.
5. Lu G. Chen, Thermo-Optical Properties of Polymer Dispersed Liquid Crystals, Science, Engineering and Technology Portfolio RMIT University, 4-5, 2007.

6. Chauhan M. and A. Doshi, Synthesis and Study of Thermotropic Mesogenic Homologous Series: p- (p'-nalkoxybenzoyloxy)-m- Chlorophenylazo-p''- Chlorobenzenes, *PharmaChemica*, 3(1), 172-180, 2011.
7. M. B. Chauhan and A. Doshi, " Study of an azoester novel homologous series: 4-[4'-n-alkoxy benzoyloxy]-3- methoxy phenyl azo- 3''- chloro benzenes ", *PharmaChemica*, 3(1), 172-180, (2011).
8. M. B. Chauhan, D. K. Bhoi, M. T. Machhar, D. K. Solanki and Dhaval Solanki, "Synthesis, characterization and mesomorphic properties of azoester mesogens: 4-nalkoxybenzoic acid 4-[3-(benzylidene-amino)-phenylazo]-phenyl ester ", *PharmaChemica*, 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 .
10. BE´ NYEI G. , JALSOVSZKY I., SLUGOVIC C., TRIMMEL G. , PELZLŠ G., VAJDA A. , E´ BER N. and FODOR-CSORBA K., "Liquid Crystals", 32 (2), 197–205, 2005.
11. Rahman M., Salisu A, Silong S. Lutfor M. and Ayub M., *Asian J. of Appl. Sci.*, 2(2), 177-183, 2009.
12. Liliana C., Csunderlik C. And Otilia C., *Chem. Bull*, 50(64), 1-2, 2005
13. Ali H. and Nasreen J., *IJRPC*, 5(4), 527-535, 2015.
14. D. Dunmur, A. Fukuda and G. Luckhurst, " Praefcke K. in *Physical Properties of Liquid Crystals. Nematics*", ed. INSPEC, London, 17–35 2001.
