



Synthesis, Characterization and Liquid Crystals Properties of New Mesogenic Azo Ester

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ABSTRACT

Two homologous series B and C of Azo Ester with Nitro Terminal, Side group Substituent compounds were synthesized. Their structures were elucidated using spectroscopic techniques such as FT- IR (Infrared), ¹H-NMR. Mesomorphic properties and phase transitions were studied using polarized hot stage optical microscopy and differential scanning calorimeter (DSC). It has been found that in series B the B₆ and B₈ are smectic and nematic mesophase compounds while in series C the C₉ is pure smectic mesophase.

Keywords: Azo ester, Smectic, Nematic, Liquid Crystals, Mesophase.

INTRODUCTION

The polarized optical microscopy and DSC used to determination the mesophase [1,2]. With development of liquid crystal science and technology more mesogenes have been prepared and study. Thermotropic L.C. is one of type of mesogenes currently extensively studied [3-6]. Most molecule structures of thermotropic mesogenes contain a rigid core compose of two or more aromatic rings connected by connective groups as azomethene CH=N, Azo N=N ester –COOR groups and other to provides a stepped core structure and maintained the molecular linearity in order to exhibit higher stability and form mesophases, The presence of aromatic rings lead to increasing of thermal range of L.C. phases through increasing of molecule Polarizability and Rigidity [7,8]. One or more flexible terminal chain which connected by rigid core by formation of ether, thioether, ester and thioester bond, In general the increasing of chain length accompanied by decreasing of melting point of mesogene [9,10]. Side groups have very important effect on L.C. properties more studies showed that the side groups (as F, Cl, Br, I, CH₃, OCH₃) when presence in the mesogene the ratio width/length of molecule will be increasing this lead to prevent the L.C. properties [11-14]. However, a literature survey indicates that liquid crystalline with azo ester contain nitro as terminal and side groups are very rare, so, in the present work, we have prepared two series compounds 1st series (B) including (E)-4-((4-Nitrophenyl)dienyl 4-(alkanoyloxy)benzoate) 2nd series (C) including (E)-4-((4-Nitrophenyl)dienyl 4-(alkanoyloxy)-3-nitrobenzoate) compounds (Figure 1) of homologous series of (B) and (C) compounds.

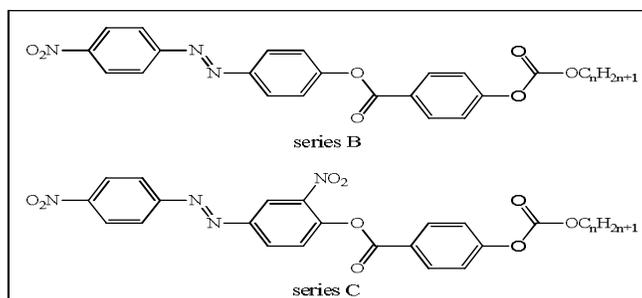


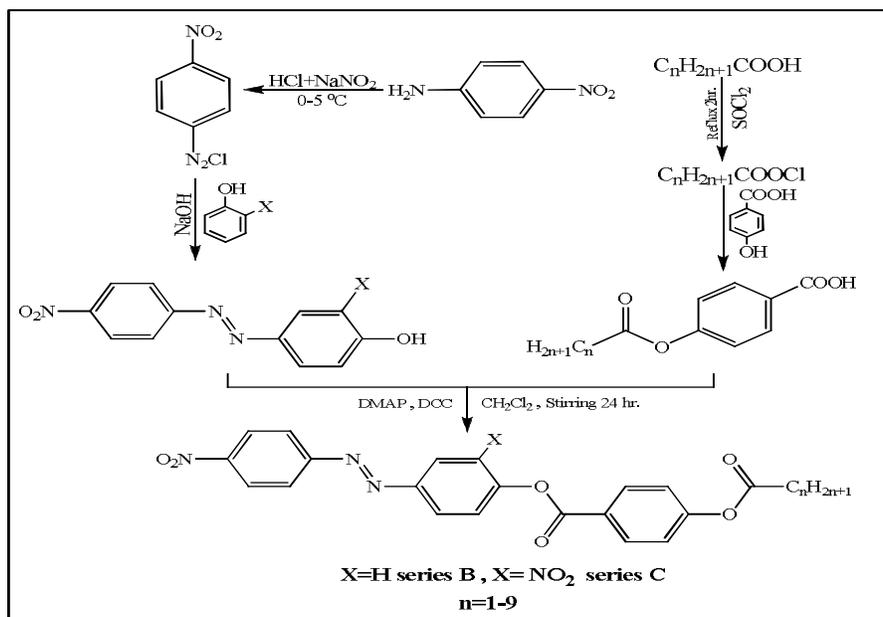
Figure 1. Structure of the studied series (B) and (C)

MATERIALS AND METHODS

General: Infrared spectra were recorded as KBr pellets on a Bruker-Tensor 27 spectrometer. $^1\text{H-NMR}$ spectra were recorded on Bruker-500 MHz spectrometer using CDCl_3 as a solvent and TMS (Tetramethylsilane $(\text{CH}_3)_4\text{Si}$) as internal standard. The phase transitions were observed with a Leitz Laborlux 12 Pol optical microscope with polarized light in conjunction with a leitz 350 hot stage equipped with a Vario-Orthomat camera of transition temperatures were made using a Shimadzu DSC-60 differential scanning calorimeter with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

Synthesis of 4-(Alkanoyloxy) Benzoic Acid series (A): 3 g *p*-hydroxy Benzoic acid (0.02 mol) was dissolved in 10.0 mL dry pyridine in a 50 mL round bottom flask. 0.022 mol acid chloride was added drop wise through separation funnel to the *p*-hydroxy Benzoic acid solution in ice bath for 1h then allowed the mixture for stirring on a stirrer at room temperature overnight. The mixture acidified with 20 mL of 10% HCl then pour the mixture on crush ice. The solid obtained filtered washed successively with distilled water, then recrystallized with ethanol.

Synthesis of Azo Compounds: Azo Compounds were prepared as reported method [15]. Azo Ester Compounds were also prepared by the reported method [15] (Scheme 1).



Scheme 1. Synthesis steps for prepared azo ester compounds

RESULTS AND DISCUSSION

4-(Alkanoyloxy)Benzoic Acid identified by FT-IR spectrophotometer all spectrum shows appear of stretching vibration for ester carbonyl group ($1754\text{-}1765\text{ cm}^{-1}$) in addition to (CO)-O and C-O bands for ester. The results are given in Table 1 [16].

Table 1. FT-IR absorption bands for series A

Comp.	n	νO-H	νC-H		νC=O		νC=C		CO-O	C-O	δO-H		γ CH ₂
			Arom.	Aliph.	ester	Carboxy					In plane	Out of plane	
B ₂	1	2500-3400	3070	2953	1758	1685	1605	1511	1291	1199	1419	919	-
B ₃	2	2500-3200	3073	2945	1758	1686	1603	1508	1292	1206	1428	935	762
B ₄	3	2500-3250	3073	2965	1758	1684	1605	1512	1276	1208	1427	929	763
B ₅	4	2500-3300	3079	2960	1757	1696	1602	1509	1291	1207	1428	934	764
B ₆	5	2500-3250	3075	2956	1755	1685	1604	1508	1292	1207	1429	933	765
B ₇	6	2500-3300	3075	2959	1765	1681	1605	1505	1287	1211	1424	948	765
B ₇	7	2500-3250	3084	2954	1754	1684	1604	1508	1291	1207	1429	929	766
B ₉	8	2500-3300	3075	2954	1754	1683	1604	1508	1291	1207	1429	926	766
B ₁₀	9	2500-3300	3078	2954	1756	1683	1601	1508	1291	1207	1429	928	764

The series B & C synthesised in accordance with Scheme 1. The FT-IR spectrums for series B compounds shows disappear of the stretching vibration of hydroxyl group and appearance of stretching vibration of ester carbonyl group ($1752\text{-}1763\text{ cm}^{-1}$) furthermore (CO)-O, C-O. The results are given in table 2 [16].

Table 2. FT-IR absorption bands for series B

Comp.	n	νC-H		νC=O ester	νC=C		νN=N	νNO _{2 sy}	CO-O	C-O	γ NO ₂	γ CH ₂
		Arom.	Aliph.									
G ₂	1	3073	2928	1763	1605	1517	1415	1349	1270	1199	754	-
G ₃	2	3073	2929	1760	1602	1523	1414	1347	1276	1203	757	720
G ₄	3	3077	2929	1757	1602	1522	1412	1347	1275	1202	755	720
G ₅	4	3072	2929	1756	1603	1520	1415	1352	1274	1210	754	722
G ₆	5	3073	2929	1755	1603	1519	1415	1353	1273	1208	764	722
G ₇	6	3073	2929	1756	1605	1507	1415	1349	1274	1203	754	722
G ₇	7	3075	2927	1752	1604	1504	1415	1350	1268	1203	754	723
G ₉	8	3075	2927	1758	1604	1504	1414	1345	1269	1201	755	721
G ₁₀	9	3074	2927	1760	1605	1500	1414	1347	1269	1202	756	720

Two compounds (B₇, B₁₀) of series B identified by ¹H-NMR spectroscopy, ¹H-NMR spectrum for B₇ shows triplet signal at δ=0.94 assigned for methyl groups for aliphatic chain, multi signal at δ=1.3-1.5 assigned for methylene groups in aliphatic chain, pentet signal at δ=1.8 assigned for β methyl group in aliphatic chain triplet signal at δ=2.6 assigned for α methyl groups for aliphatic chain, aromatic hydrogen observed as multi signal at δ=7.1-8.45. The results are given in table 3 [16].

Table 3. Chemical shift for B₇, B₁₀ Compounds

Comp.	n	CH ₃	CH ₂	βCH ₂	αCH ₂	Ph.Ring
B ₇	6	0.94 t	1.3-1.5 m	1.8 p	2.6 t	7.1-8.45 m
B ₁₀	9	0.93 t	1.0-1.5 m	1.80 p	2.53 t	7.28-8.43 m

The FT-IR spectrums for series C compounds shows disappear of the stretching vibration of hydroxyl group and appearance of stretching vibration of ester carbonyl group ($1741\text{-}1744\text{ cm}^{-1}$) furthermore (CO)-O, C-O. The results are given in table 4 [16].

Table 4. FT-IR absorption bands for series C

Comp.	n	νC-H		νC=O ester	νC=C		νN=N	νNO ₂ Sy	CO-O	C-O	γ NO ₂	γ CH ₂
		Arom.	Aliph.									
C ₂	1	3084	2928	1743	1605	1525	1415	1343	1261	1201	755	-
C ₃	2	3085	2929	1742	1620	1525	1426	1343	1262	1201	755	763
C ₄	3	3079	2935	1742	1601	1530	1414	1346	1262	1203	752	720
C ₅	4	3079	2930	1742	1601	1529	1414	1346	1262	1205	751	719
C ₆	5	3080	2929	1742	1607	1534	1412	1343	1269	1204	755	732
C ₇	6	3036	2929	1744	1605	1534	1414	1343	1271	1206	755	734
C ₇	7	3079	2935	1741	1602	1529	1414	1345	1264	1205	751	720
C ₉	8	3036	2929	1744	1605	1535	1414	1344	1271	1207	756	735
C ₁₀	9	3035	2928	1741	1627	1536	1414	1344	1272	1163	754	725

Series C compounds identified by ¹H-NMR spectroscopy, ¹H-NMR spectrum for C₇ shows triplet signal at δ=0.8 assigned for methyl groups for aliphatic chain, multi signal at δ=1.3-1.4 assigned for methylene groups in aliphatic chain, multi signal at δ=1.5-1.78 assigned for β methyl group in aliphatic chain triplet signal at δ=0.8 assigned for α methyl groups for aliphatic chain, aromatic hydrogen observed as multi signal at δ=7.1-8.4. The results are given in table 5 [16].

Table 5. chemical shift for C₇,C₁₀ Compounds

Comp.	n	CH ₃	CH ₂	βCH ₂	αCH ₂	Ph.Ring
H ₇	6	0.8 t	1.3-1.4 m	1.5-1.78 m	2.6 t	7.1-8.4 m
H ₁₀	9	0.9 t	1.2-1.45 m	1.65-1.8 m	2.59 t	7.0-8.5 m

The DSC scans carried out on these compounds show transitions at temperatures which are in agreement with those obtained by optical microscopy. The phase transition temperatures of series B compounds showed that two compounds B₆ and B₈ exhibit liquid crystals properties smectic and nematic mesophase. The results are given in table 6, figure 2 reflects the Sm and N phases for B₆ and B₈ mesogenes.

Table 6. The phase transitions of series B compounds (°C).

Comp. symb.	B ₂	B ₃	B ₄	B ₅	B ₆	B ₇	B ₈	B ₉	B ₁₀
n	1	2	3	4	5	6	7	8	9
Cr→Sm	-	-	-	-	124.05	-	206.32	-	-
Sm→N	-	-	-	-	313.17	-	272.06	-	-
N→I	-	-	-	-	346.63	-	311.42	-	-
ΔT _{Sm}	-	-	-	-	189.12	-	65.74	-	-
ΔT _N	-	-	-	-	33.46	-	39.36	-	-

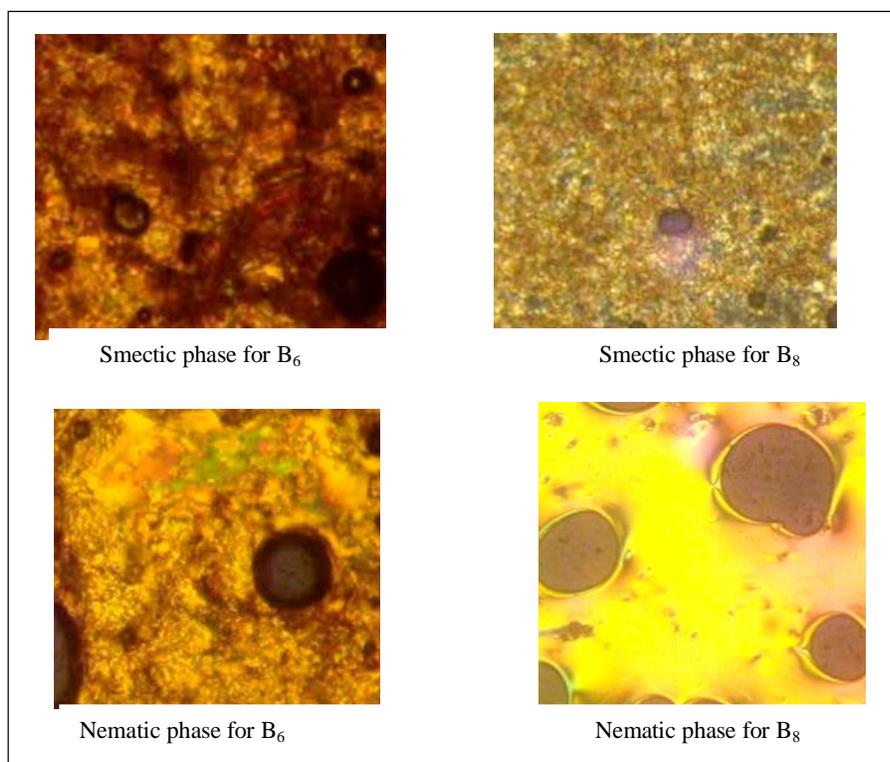


Figure 2. Sm and N phases for B₆ and B₈ mesogenes

While the phase transition temperatures of series C compounds showed that one compounds C₉ exhibit liquid crystals properties smectic mesophase only. The results are given in table 8, figure 3 reflects the smectic texture for C₉ mesogene.

Table 7. The phase transitions of series C compounds (°C).

Comp. symb.	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀
n	1	2	3	4	5	6	7	8	9
Cr→Sm	-	-	-	-	-	-	-	166.30	-
Sm→I	-	-	-	-	-	-	-	235.90	-
ΔT _N	-	-	-	-	-	-	-	69.6	-

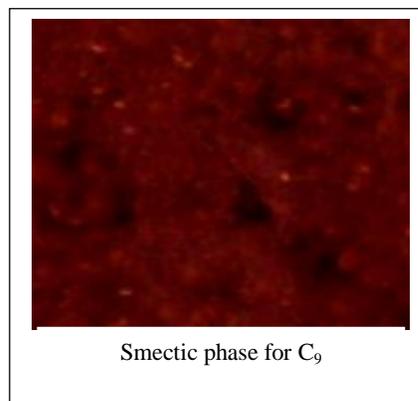


Fig 3.

APPLICATIONS

This study is useful for knowing the effect of nitro as side and terminal group on the L.C. properties.

CONCLUSIONS

New azo ester mesogenic compounds with nitro side group on the central benzene nucleus were synthesized. The study indicated that the type of lateral groups and their position adversely affects the mesomorphic properties of these compounds.

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