

Study of Novel Liquid Crystalline Materials with Lateral Ester Group

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Abstract:- Novel twelve homologues having azolinkage of series 4- Methyl -[3'- carbethoxy -4' (4''-n-alkoxy benzyloxy)] azobenzenes have been synthesized. The first member of the series is nonmesogenic. The ethyl to n-dodecyl homologues exhibit enantiotropic nematic mesophases. The n-tetradecyloxy and n-hexadecyloxy homologue exhibit monotropic smectic mesophases. The plot of transition temperatures versus number of carbon atoms in alkoxy chain shows usual falling tendency for the nematic- isotropic transition temperatures. The mesogenic behaviour of present series is explained by comparing its homologue with other homologue of related mesogenic series. The synthesised compounds are characterised by combination of elemental analysis and standard spectroscopic methods. For the exhibition of mesomorphic property the role of ester and azo linkages has been discussed. The impact of lateral carbethoxy group on mesomorphism is also discussed.

Keywords : Liquid crystals , mesomorphic , smectic , nematic , monotropic .

INTRODUCTION

Liquid-crystalline materials, either low molar mass or polymeric in nature, containing an azo group in the mesogenic core, are often studied from the point of view of their interesting optical properties, which enable application in, for example, optical switching, holography, and optical storage devices [1–6]. Azo dyes are also being used in liquid-crystal display devices for the guest–host interaction [7]. Aromatic azo-containing compounds (Ar-N=N-Ar') can undergo a much easier photoinduced trans-cis isomerization than the C=C bond and thus can generate more interesting photoactive liquid crystals (LCs). Among these photoactive mesogenic units, azobenzene derivatives are most extensively investigated. The rigid rod-like structure of azobenzene molecules makes them suitable candidates for exhibiting liquid crystallinity [8,9]. On the other hand, the unique characteristics of azobenzene molecules provide the possibility of molecular motion in response to light or heat and thus offer many opportunities in photonic applications.

Thermotropic mesomorphic substances exhibit mesomorphism based on the variations of temperature and the range of temperature depending upon their individual molecular rigidity and flexibility [10–11] generated from respective molecular structure. For potential commercial applications, the existence of mesophases at lower temperatures is of very high importance. Lateral

substituents play an important role in order to decrease the phase transition temperatures. Much work has been reported on different short lateral substituents till now. However literature survey shows that a lateral ester group has not been exploited much, therefore, in the present work an attempt has been made to study and establish the effect of lateral ester group on mesomorphism. We report, design and synthesis of novel mesogenic homologous series with three phenyl rings in the main core linked through ester and azo central linkages and substituted by a lateral –COOCH₃ group on the central benzene ring, and investigated the influence of lateral ester group on mesomorphism.

2. EXPERIMENTAL

2.1 Synthesis

4-Hydroxy benzoic acid, n-alkyl halides, thionyl chloride, pyridine, methanol, potassium hydroxide, methyl salicylate, 4-methyl aniline and sodium nitrite were chemically pure of lab grade. Solvents were dried and distilled prior to use.

1. 4-n-Alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by the modified method of Dave and Vora [12].
2. 4-hydroxy-3-carbomethoxy-4'-methyl azobenzene (DA-1) was synthesized by known method [13].
3. The series namely 4-methyl-[3' carbomethoxy -4'(4''-n-alkoxy benzyloxy)] azobenzene was synthesized by adding dropwise the solution of 4-hydroxy-3-carbomethoxy-4'-methyl azobenzene (DA-1) in dry pyridine to the respective solution of 4-n-alkoxy benzoyl chloride at 0-5°C. The mixture was allowed to stand overnight at room temperature. It was acidified with cold 1:1 aqueous hydrochloric acid and the separated solid was washed successively with dilute sodium hydroxide solution and water. The final product obtained was recrystallized several times from glacial acetic acid until constant transition temperatures were obtained which are recorded in Table 1. The elemental analysis of each compound was found to be satisfactory and shown in Table 2. The route of synthesis of series 1 is illustrated in Scheme 1.

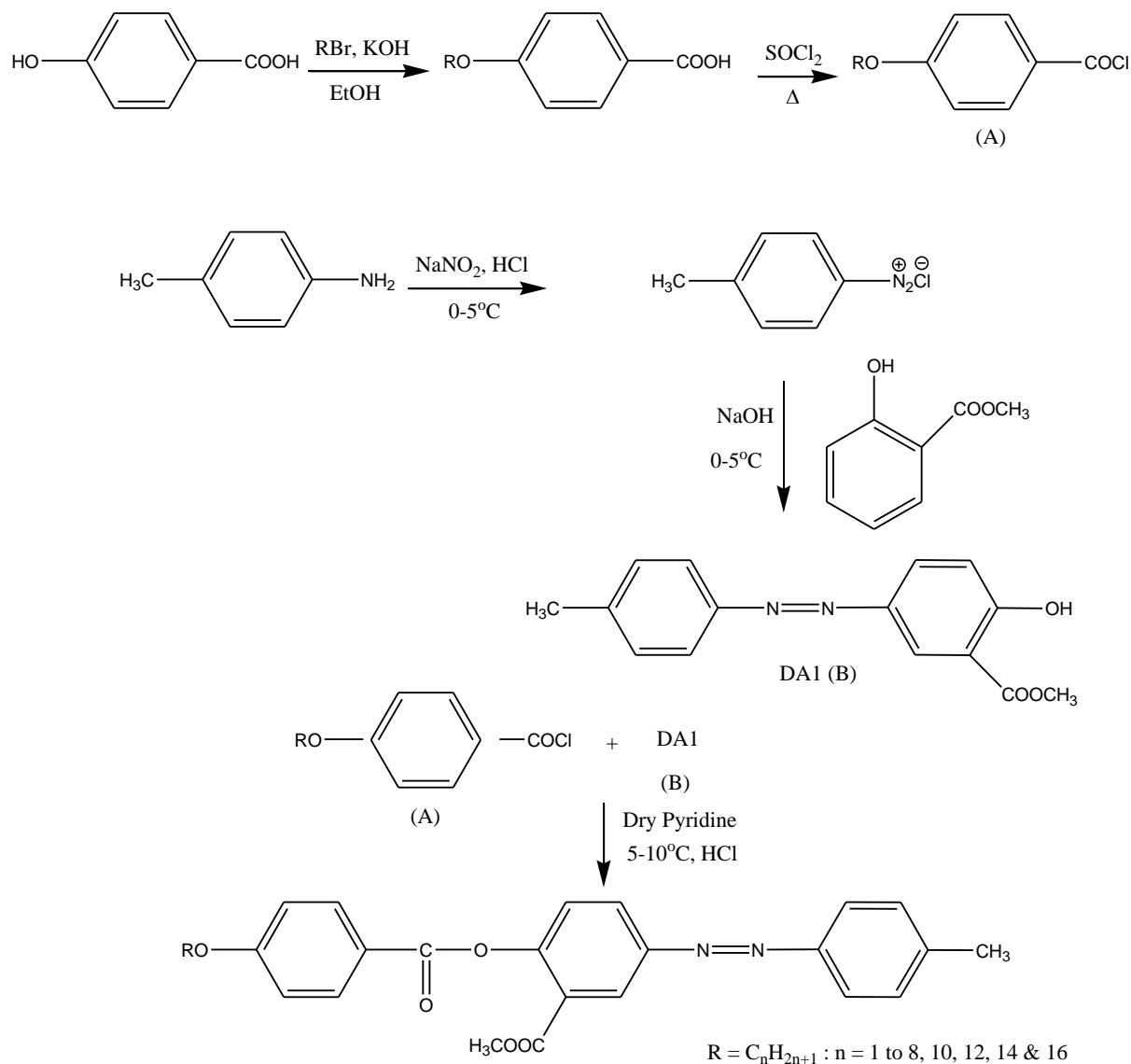
2.2 Characterization

Micro analysis of the compounds was performed on a Coleman carbon, hydrogen analyser. FTIR spectra were determined on Nicolet impact 400 FTIR using Nujol. ¹H

NMR spectra was performed on Perkin-Elmer (90 MHz) spectrometer using tetra methylsilane (TMS) as internal reference substance and CDCl_3 as solvent. Liquid

crystalline properties were determined on a Leitz Laborlux 12 POL microscope equipped with a heating stage.

The synthetic route to the series is mentioned below in scheme-1



Scheme 1: The route of synthesis of series 1 compounds

Table 1 Transition temperatures (°C) of Series I

n-Alkyl C _n H _{2n+1} n=		Group	Transition temperatures (°C)		
Compound No.	Series I	Sm C	N	I	
1	1	--	--	175	
2	2	--	155	172	
3	3	--	135	158	
4	4	--	119	155	
5	5	--	108	143	
6	6	--	106	136	
7	7	--	105	130	
8	8	--	103	125	
9	10	--	83	116	
10	12	--	93	110	
11	14	(93)*	--	105	
12	16	(98)	--	106	

*value in parenthesis indicate monotropy

Sm C- Smectic , N- Nematic , I-Isotropic

Table – 2 Elemental analysis for ethyloxy, butyloxy , octyloxy and decyloxy derivative

Molecular formula	Element % found	(compared with % calculated)	
C	H	N	
C ₂₄ H ₂₂ O ₅ N ₂	68.54 (68.89)	5.33 (5.26)	7.08 (6.69)
C ₂₆ H ₂₆ O ₅ N ₂	69.72 (69.95)	5.57 (5.82)	6.60 (6.27)
C ₃₀ H ₃₄ O ₅ N ₂	71.93 (71.71)	6.93 (6.77)	5.37 (5.57)
C ₃₂ H ₃₈ O ₅ N ₂	72.60 (72.45)	6.95 (7.16)	5.63 (5.28)

2.3 Analytical Data

FTIR (Nujol) Spectra cm⁻¹ . n-Butoxy Derivative : 3000 (C-H Str. Aromatic), 2900, 2850 (C-H Str. Aliphatic), 1705 (C=O Str. Ester), 1600 (N=N Str. Azo), 1370, 1270, 1160 (aryl ether), 1060, 960, 890, 760. n-Decyloxy derivative : 2950 (C-H Str. Aromatic), 2900, 2850 (C-H Str. Aliphatic), 1700 (C=O Str. Ester) , 1600 (N=N Str. Azo) ,1370, 1250, 1150 (aryl ether) , 1050, 900, 860, 700.

Proton NMR spectra in δ PPM (Solvent CDCl₃ 90 MHz, standard TMS). n-Decyloxy derivative : δ 0.9 (t, 3H, CH₃) , 1.1-1.75 (s, 16 H, Ar-O-(CH₂)₈-) , 2.4 (s, 3H, CH₃), 3.7(s, 3H, CH₃ of ester), 4.0 (t, 2H of Ar-OCH₂), 6.95 – 8.05 (m, 11H, Ar-H).

3. RESULTS AND DISCUSSION

The homologous series 4-Methyl-[3'-carbethoxy-4'-(4''-n-alkoxybenzoyloxy)] azobenzenes consisting of twelve homologues. The first member of the series is nonmesogenic in nature. The ethyl to n-dodecyl homologues exhibit enantiotropic nematic mesophases. The n-tetradecyloxy and n-hexadecyloxy homologues exhibit monotropic smectic mesophases. The transition temperatures are plotted versus the number of carbon atoms in alkyl chain of n-alkoxy terminal end group and are recorded in Table1. The phase diagram showing phase behaviour is depicted in Figure 1. The nematic-isotropic transition curve shows falling tendency as series is ascended .The nematic phase lengths vary from 17 ° to 36 °C .

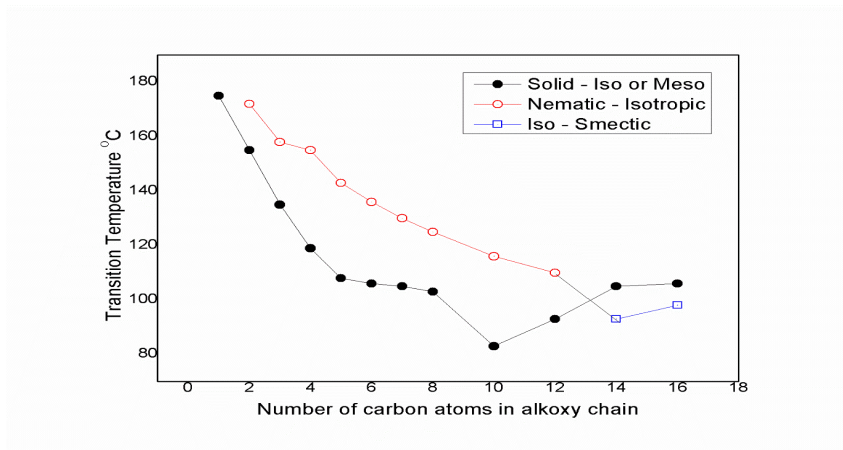


Figure 1. The Phase behaviour of series

There is close relationship between mesomorphism and molecular constitution of organic compounds. Hence thermal stability, a measure of mesomorphism, can be correlated with the molecular constitution of the compounds. Figure 2 shows the transition temperatures and

molecular structures of the n-Octyloxy derivative and n-Dodecyloxy derivative (compound 8 and 10 respectively) of the present series I and the structurally related compound A [14], and B [15] reported in literature.

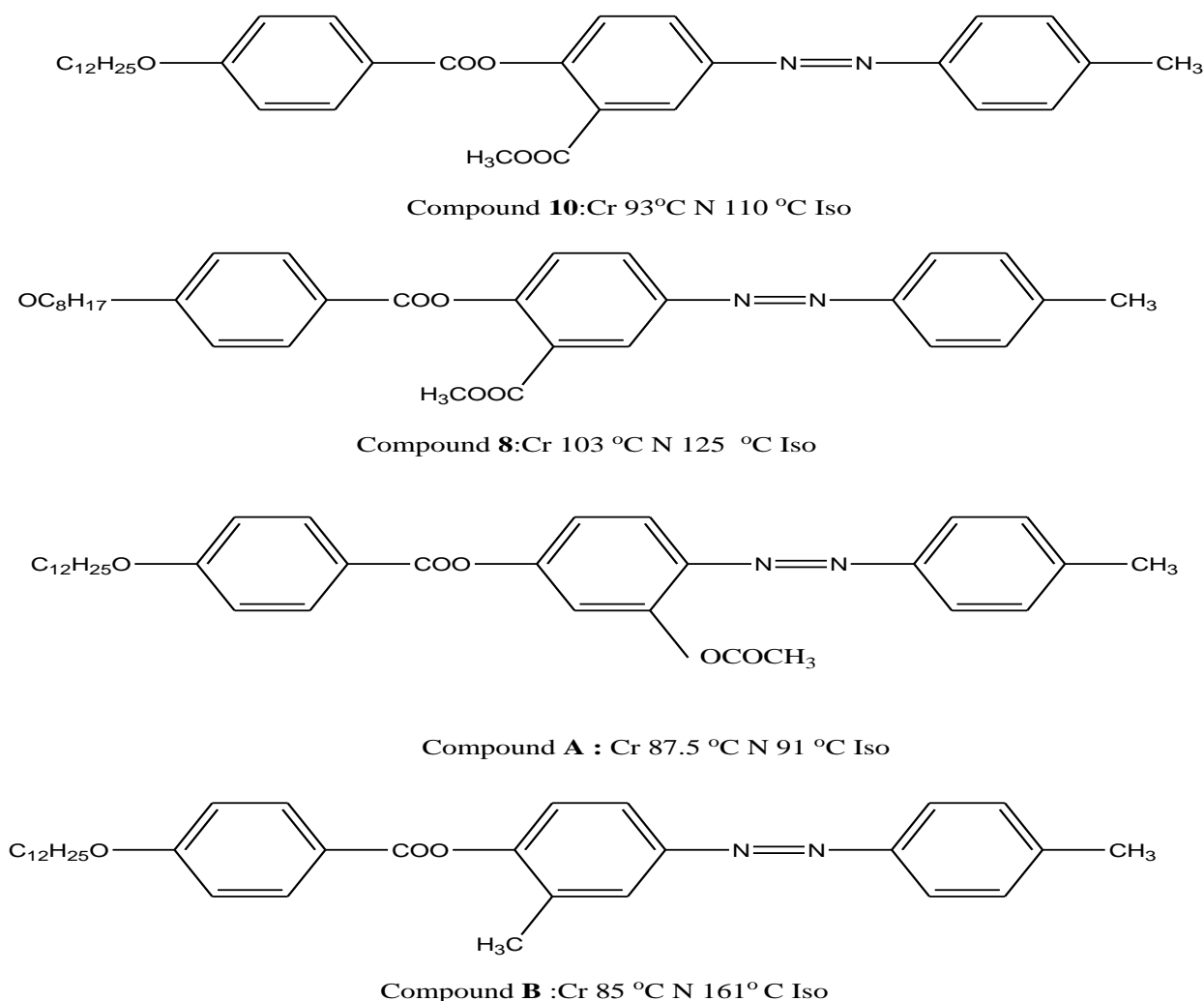


Figure 2: Comparative molecular geometries of compounds 8, 10 , A and B

The reference to figure 2 shows that molecules of compound 10 (C₁₂ homologue) of the present series and compound A possess similar molecular geometries except difference in lateral substituents. It is a -COOCH₃ group ortho to an ester linkage in compound 10 and -OCOCH₃ group ortho to rigid azo linkage in compound A. Both compounds exhibit only nematic mesophases. However, nematic phase length and thermal stability of compound 10 is higher by 11.5°C and 19°C respectively than that of compound A. The lateral groups in both compounds are polar in nature and almost similar in size, but are behaving differently. The overall effect of acetyloxy group generating from its attractive forces due to its ortho position to rigid azo group in compound A resulting into lowering of nematic phase length and thermal stability as compared to compound 10. This is an interesting observation that slight change in the lateral position of substituent, affects the mesophases length and thermal stability greatly.

On comparing compound 8 (C₈ homologue) of present series and compound B, shows that both compounds exhibit nematic mesophases, however the nematic phase length and thermal stability of compound B is higher by 51°C and 36°C respectively than those of compound 8. This can be due to the fact that there is a short -CH₃ group in lateral position in compound B whereas compound 8 has a long -COOCH₃ group at that position. Long and bigger lateral ester group increases the breadth of the molecules of compound 8 and changes the molecular conformation, which decreases the nematic phase length and thermal stability of compound 8 than that of compound B. Gray [16] has explained that an increase in the breadth of the molecules reduces mesophases length and thermal stability. In the present series SmC (Schlieren texture) and nematic (Marble structure) are inferred from the textures observed under a polarizing microscope.

CONCLUSION

In this paper, we have presented the synthesis and characterization of a novel mesogenic homologous series viz. 4-Methyl-[3'carbethoxy-4'-(4''-n-alkoxybenzoyloxy)] azobenzenes. The series is found to be predominantly nematogenic in nature where, members up to n-dodecyloxy derivative exhibit nematic mesophases and only n-tetradecyloxy and n-hexadecyloxy derivatives exhibit monotropic Smectic C mesophases. The study revealed that introduction of lateral ester group increases the breadth of molecule and decreases the phase length and thermal stabilities of nematic mesophases and has been found to be less conducive for the formation of smectic mesophases.

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