



Novel Thermotropic Liquid Crystals with Lateral Aryl Substituent

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Abstract

A novel mesogenic homologous series 4 - carbethoxy 2', 4'-bis (4''-n-alkoxy benzyloxy) azobenzenes has been synthesized by fixing a rigid 4- carbethoxy phenyl azo group to a resorcinol moiety and both the phenolic hydroxyl groups are esterified by 4-n alkoxy benzoyl groups. The lower homologues of the series exhibit monotropic smectic mesophases whereas the higher homologues exhibit enantiotropic smectic mesophases. The synthesized compounds were characterized by a combination of elemental analysis and IR and NMR spectroscopy. Their mesomorphic properties are discussed and compared with those of structurally related homologous series. The impact of the lateral aryl segment on mesomorphism is also discussed.

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

Introduction

Liquid crystalline materials are found to have an important role in new and emerging electro-optical technologies. Thermotropic liquid crystals consists of either linear or disc-like organic molecules. The general architecture for linear thermotropic liquid crystals consists of linearly linked ring systems and flexible chains, the permanent dipoles and polarisable moieties also being requirements. The rings may be linked to each other either directly or through some linking group (e.g. ester, olefinic, acetylenic, azo, azoxy, dimethylene or oxymethylene) that maintains the linearity of the core¹. The flexible alkyl chains may be linked either directly with the ring or through the intervening hetero atoms such as oxygens, sulphur and nitrogens. These polar groups may also impart dielectric anisotropy to the molecules². The thermal stability of the mesophase is determined by the nature of the molecule, steric and electronic factors. It has also been reported in the literature³⁻⁵ that the linking units capable of maintaining the rigidity and linearity of the molecule also promote mesophase stability. The aromatic esters are known for their thermal stability, easy synthesis and relative resistance to hydrolysis. Azobenzene derivatives are very effective for controlling liquid crystals by light, because the geometrical change due to photo-isomerisation gives a concomitant change in chemical and physical properties not only in the azobenzene residue but also in the environment around it. Such photonic control has mainly been applied in the nematic phase by means of a transmission, reflection and light scattering mode. The photo-responsive properties of azobenzene derivatives due to photo-isomerisation have also been reported⁶⁻¹⁰. It is reported that the addition of chromophores such as azo groups are found the lower energy required in optical field¹¹. These features have made azo compounds, promising candidates for optical applications.

Lateral substitution play an effective role in the mesogenic properties of the compounds. Studies on the effect of lateral substitution have been carried out by several researchers. Recently we have also reported work on lateral hydroxy and methyl substituents and observed that lateral substitution in the mesogenic core of the molecules causes reduction in the mesophase thermal stabilities¹²⁻¹³. But the effect of lateral aromatic branch on type of liquid crystals formed is quite different¹⁴. A number of homologous series containing aromatic branch at the lateral position of the mesogenic core have been reported in literature¹⁵⁻¹⁷. Such laterally aryl substituted mesogens form a group which possesses molecular geometry in between that of calamitic liquid crystals and discotic liquid crystals. Hence, molecules possessing such a structure are interesting to synthesize as this would help in understanding the relationship between mesomorphism and molecular geometry.

With this in view, we have synthesized a homologous series containing three rings in the main core linked through ester and azo central linkages and substituted by a lateral aromatic branch on the central benzene ring, and investigated the influence of the lateral aromatic branch on mesomorphism.

Material and Methods

4-Hydroxy benzoic acid, n-alkyl halides, thionyl chloride, pyridine, methanol, potassium hydroxide, resorcinol, ethyl 4-amino benzoate, and sodium nitrite were chemically pure of lab grade. Solvents were dried and distilled prior to use. The micro analysis of the compounds was performed on a Coleman carbon, hydrogen analyser. FTIR spectra were determined on Nicolet impact 400 FTIR. ¹H NMR spectra was performed on Perkin-Elmer (90 MHz) spectrometer using tetra methylsilane (TMS) as internal reference substance and CDCl₃ as solvent and the chemical shift values recorded as δ (ppm units) Liquid

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

Synthesis of compounds: 4-n-Alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by the modified method of Dave and Vora¹⁸. 4-Carboxy-2'-4'-dihydroxy azobenzene (DA-1) was synthesized by known method¹⁹.

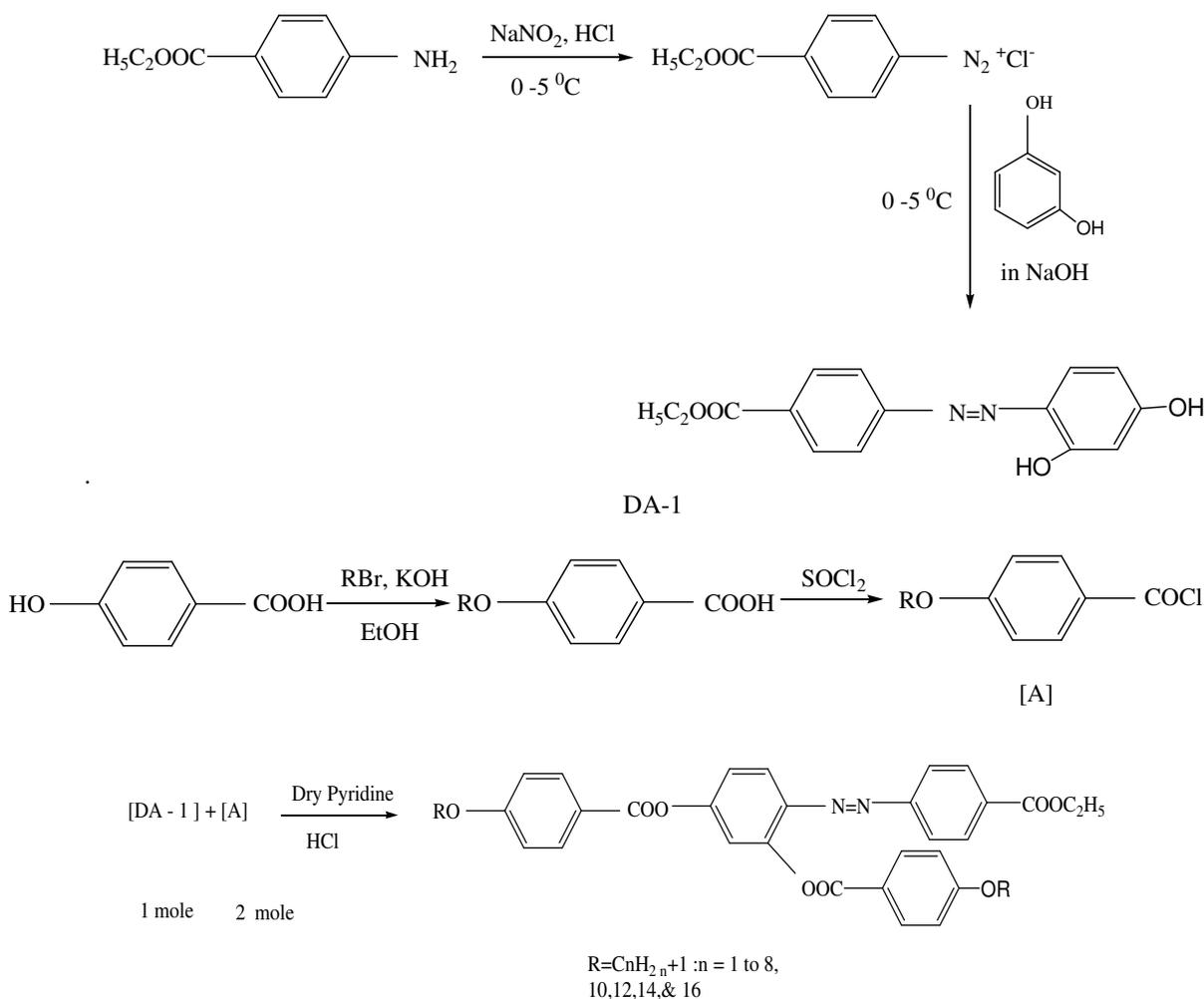
The series namely 4-Carboxy-2'-4'-bis (4''-n- alkoxy benzyloxy) azobenzene was synthesized by adding dropwise one mole solution of 4-Carboxy-2'-4'-di hydroxy azobenzene (DA-1) in dry pyridine to the respective two moles solution of 4-n- alkoxy benzoyl chloride at 0-5°C. The mixture was allowed to stand 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 recorded in table-2. The route of synthesis of series I compounds is illustrated in scheme-1.

Spectral Data: FTIR (Nujol) Spectra cm^{-1} n-C₃H₇ homologue : 2900 (C-H Str. Aromatic) , 2800, (C-H Str. Aliphatic), 1725 (-C=O Str, Ester), 1600(-N=N- Str. Azo), 1360, 1270, 1160 (Aryl ether) , 1050, 850, 750.

¹H NMR (CDCl₃), n-C₃H₇ homologue : δ ppm 1.15 (t, 6H 2 x CH₃), 1.5 (t, 3H, CH₃), 1.75 – 2.1 (m, 4H, 2 x CH₂), 4.1 (t, 4H of Ar O-CH₂), 4.4 (q, 2H of Ar-COOCH₂), 6.95 -8.1 (m, 15H, Ar H).

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



Scheme 1
 Synthetic route to series I compounds

Table-1
Transition Temperatures (°C) for series I compounds

Compound no	R = C _n H _{2n+1} n =	Smectic C	Isotropic
1	1	–	139
2	2	–	127
3	3	–	140
4	4	–	122
5	5	(46)*	107
6	6	(36)	112
7	7	(40)	122
8	8	(46)	100
9	10	64	85
10	12	56	85
11	14	64	82
12	16	57	67

*values in parenthesis indicates monotropy.

Table-2
Elemental analysis for ethyloxy, hexyloxy, decyloxy and tetradecyloxy derivative

Molecular formula	Element % found (compared with % calculated)		
	C	H	N
C ₃₃ H ₃₀ O ₈ N ₂	68.36 (68.04)	5.54 (5.15)	4.62 (4.81)
C ₃₇ H ₃₈ O ₈ N ₂	70.92 (70.89)	6.19 (6.62)	4.40 (4.03)
C ₄₁ H ₄₆ O ₈ N ₂	72.56 (72.95)	7.48 (7.69)	3.81 (3.47)
C ₄₅ H ₅₄ O ₈ N ₂	74.90 (74.50)	8.95 (8.49)	3.30 (3.05)

Results and Discussion

In the present work, twelve homologues of the series I (4 – Carbethoxy [2', 4'–bis (4''-n-alkoxy benzoyloxy)] azo benzenes were synthesized and evaluated for their mesomorphic properties. The first four members of series are non-mesogenic in nature. The n-pentyloxy to n-octyloxy derivatives exhibit smectic C mesophases in the monotropic form whereas the n-decyloxy to n-hexadecyloxy derivatives exhibit enantiotropic smectic C mesophases.

Figure 1 shows the plot of transition temperatures versus number of carbon atoms in alkoxy chain. The solid- isotropic or mesomorphic transition curve shows odd-even effect up to the n-heptyloxy derivative and then falls as series is ascended. The isotropic - smectic transitions curve rises up to the n- octyloxy derivative and then falls smoothly for higher members.

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-decyloxy derivative (compound 9) of the present series I and the structurally related compounds A²⁰, B¹⁶ and C¹⁷ reported in

literature. The molecular geometries of all the compounds under comparison have three phenyl rings joined through an ester and azo central linkages with n-alkoxy groups at the left terminals and flexible lateral aromatic branches at the middle phenyl rings. The right end terminal groups are –COOC₂H₅, –COCH₃, –CH₃ and –OC₂H₅ for compounds 9, A, B and C respectively. The different mesomorphic properties arises due to the presence of different right terminal groups which differ in their sizes and polarities.

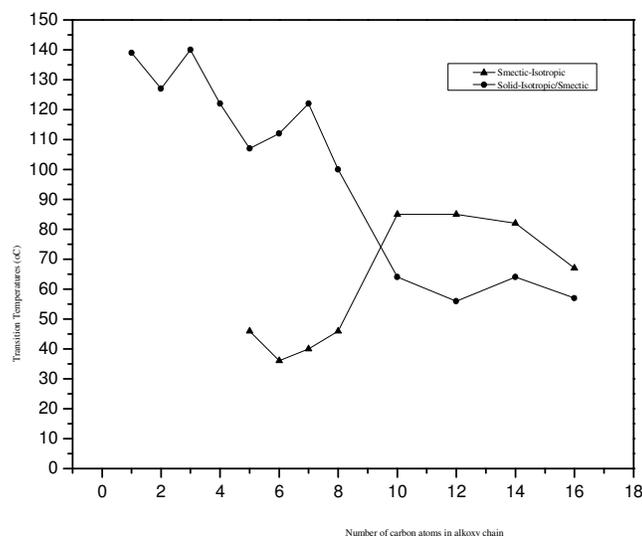


Figure-1
The plot of transition temperatures versus number of carbon atoms in alkoxy chain

On comparing compound 9 and A, it is observed that compound 9 exhibits enantiotropic smectic C mesophase whereas compound A is enantiotropic nematogen. The molecules of compounds 9 and A differ only in the right terminal groups. The compound 9 has –COOC₂H₅ group while compound A has –COCH₃ group at that position. The long –COOC₂H₅ group in compound 9 aids the formation of smectic mesophase due to enhanced lateral attraction as compared with terminal attractions, which facilitates lamellar packing required for the formation of the smectic mesophase²¹. The presence of short terminal acetyl group in compound A enables the significant forces of attraction which serve to stabilize parallel orientation by end to end molecular attractions required for the formation of nematic mesophase.

Comparison of compound 9 with compound B shows that compounds 9 exhibits enantiotropic smectic mesophase, while compound B exhibits monotropic smectic phase. The type and polarity of terminal groups behaves differently for both the compounds. The molecules of compound 9 is longer and polarisable due to presence of long and highly polar –COOC₂H₅ group at the terminal end as compared with short

and nonpolar $-CH_3$ group in compound B at that position. The increased length and polarity of compound 9 enhances mesogenic properties and thermal stability, and favors formation of enantiotropic smectic mesophase.

Figure 2 further shows that there is not much difference in the mesogenic properties of compounds 9 and C. Both compounds exhibit only monotropic smectic mesophases at almost similar

temperature ranges. This is quite natural as both compounds differ only in the terminal groups, other structural features are being the same. The molecules of the compound 9 have $-COOC_2H_5$ terminal group and in the case of compound C, it is $n-OC_2H_5$ group. It seems that high polarity of carboxy group matched in overall lateral cohesive forces exerted by n-ethoxy group which imparts sufficient polarizability to exhibit smectic mesophase at almost same temperature ranges.

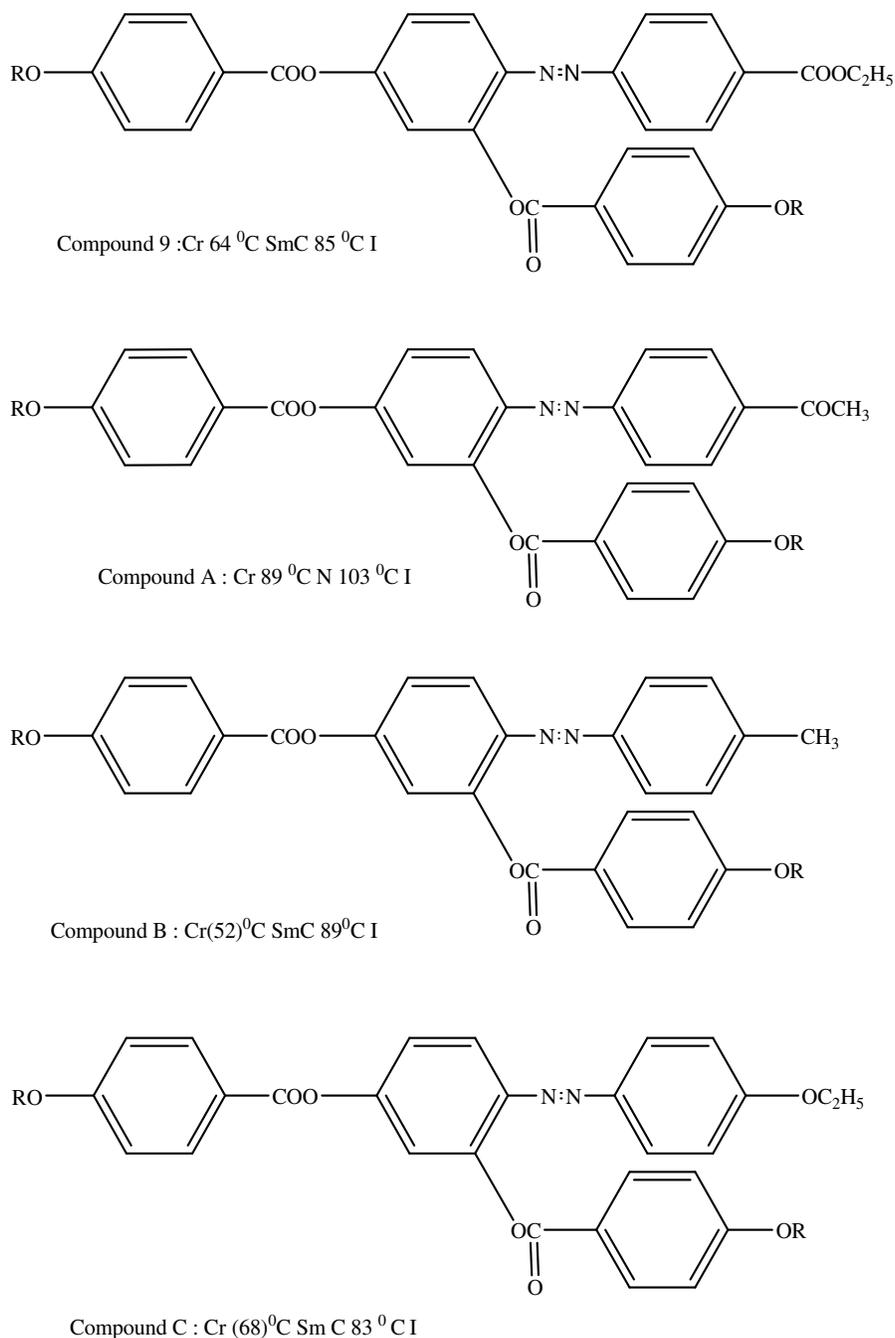


Figure -2

The comparative molecular structures and transition temperatures of compound 9, A, B and C

Conclusion

A novel homologous series of azomesogens containing long chain lateral aryl substituent have been synthesized. Presence of lateral long chain aryl substituent has been found to induce low melting smectic mesophases. This is a unique feature. Normally a lateral substituent is not conducive to smectogenic character. Present study has also revealed that minor changes in a mesogenic system affects the type of the mesophases. Moreover the geometry of the molecules play very important role in the close packing of smectic mesophases. An increase in flexibility may destroy the smectic phase in a system. The study provided hosts of a low melting smectic C mesogens which can be useful for application.

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