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Mesomorphic Properties of a New Homologous Series: 4-(4'-n-alkoxy benzoyloxy)-3-methoxy phenyl azo-4''-chlorobenzenes

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ABSTRACT

A homologous series with carboxylate (-COO-) and azo (-N=N-) as central groups have been synthesized by treating 4-n-alkoxy benzoyl chloride with 4-Hydroxy-3-methoxy phenyl azo-4'-chlorobenzene. The first and second members of the series are non-mesomorphic. The nematic property is exhibited by the propyl to hexadecyl derivatives. Polymesomorphism commences from Butyl derivative of the series enantiotropically. The mesogenic properties of the present series are compared with those of other structurally similar mesogenic series. Odd-even effect is observed for smectic nematic and nematic isotropic transition curve behaving in normal manner. Mesomorphic range is between 26^{0C} to 64^{0C} and series is of middle ordered melting type without any predominancy of either smectic or nematic property. Texture of nematic mesophase is of threaded type and that of smectic mesophase is focal conic fan shaped of the type Smectic-A or Smectic-C as determined by missibility method. analytical data support the structures of molecules. Transition temperatures are determined by hot stage polarizing microscope.

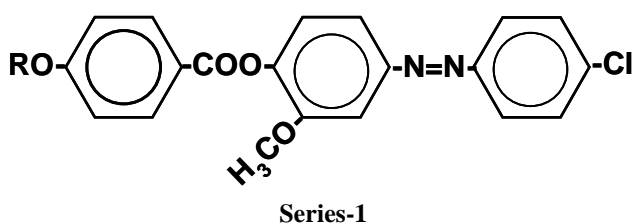
Key words: Liquid Crystals, Mesogens, Mesomorphic, Nematic, Smectic.

INTRODUCTION

Low temperature range of liquid crystals have received a thrust of their increasing demands in different fields of applications. Obviously the search for new liquid crystalline substances have a similar impact. In present investigation a new homologous series of mesogens have been synthesized and its mesomorphic characteristics have been determined.

The azoester derivatives have great potential for applications in non linear optics¹. A vast number of homologous series containing azo and ester central linkages with phenyl moiety as core system have been reported²⁻⁴. A number of homologous series with different molecular structure are reported⁵⁻⁸ in order to establish the correlation between chemical constitution and mesomorphism. In present investigation methoxy group is introduced as lateral and chloro as terminal substituent. In order to study the effect of lateral substitution (methoxy group) on range of liquid crystallinity, mesomorphic properties and degree of mesomorphism.

The transition temperatures are plotted versus the number of carbon atoms in n-alkyl chain. The effect of lateral methoxy group has not been extensively studied. This has prompted to carry out the present works.



MATERIALS AND METHODS

All chemical used for the synthesis were of reagent grade and the intermediates prepared as per known literature procedure. Elemental analysis were performed on a perkin elmer-2400, CHNS/O Analyser and the values obtained are in close agreement with those calculated. IR spectra were determined via KBR pellets using a shimadzu IR-408 spectrometer. ¹H NMR spectra were obtained with a perkin Elmer-32 spectrometer using tetramethyl silane (TMS) as an internal reference standard. The chemical shifts are quoted as δ (part per million) down field from the reference. CDCl₃ was used as a solvent for all the compounds. Liquid crystalline properties were investigated on a Leitz labour Lux 12 pol microscope provided with a heating stage. The synthetic route to the present series is illustrated in the figure-3.

2.1. Synthesis :-

2.1a. 4-Hydroxy-3-methoxy phenyl azo -4'-chlorobenzene (A).

This compound was synthesized by using conventional method of diazotization and coupling¹⁰.

2.1b. 4-n-alkoxy benzoyl chlorides (B) :-

n-Alkoxy benzoic acid refluxed with freshly distilled thionyl chloride till evolution of hydrogen chloride and SO₂ gas ceased. Excess of thionyl chloride is removed by distillation. Thus, synthesis is carried out by the method of vora et al¹¹.

2.1c. General procedure for synthesis of title homologous series :-

Compound (A) was dissolved in dry pyridine (15ml) and added slowly in portion into alkyl benzoyl chloride with shaking. Then product was warmed in hot water bath for half an hour and kept over night. Then acidified with cold 1:1 aqueous hydrochloric acid. The solid was separated, washed with dilute sodium hydroxide solution and then washed with distilled water and then dried. Finally the products were crystallized from alcohol till constant transition

temperatures determined using hot stage polarizing microscope as recorded in table -1. The analytical data supports the structures of molecules. (Table-2).

RESULT AND DISCUSSION

Homologous series 4-hydroxy-3-methoxy phenyl azo-4'-chlorobenzenes is a nonliquidcrystal substance but linking of phenyl ring bridged through -COO- and left n-alkoxy terminal induces mesomorphic character. The transition temperatures of the homologous series are shown in table-1. The first and second member of the homologous series are non-mesomorphic in nature because molecules of the same do not arrange themselves either as parallel to each other or in sliding layered structure floating condition while supper cooling the isotropic liquid. The mesomorphic^{12,13,14,15} property is exhibited from the propyl derivatives in which propyl to hexadecyl derivatives are enantiotropically nematogenic while smectic property is exhibited with nematic property by butyl to hexadecyl derivatives enantiotropically.

The transition temperatures are plotted versus the number of carbon atoms in n-alkyl chain of the left n-alkoxy terminal group of the homologues as shown in phase diagram (Figure-1). Smooth curves are drawn through points for like or related transitions. The solid-mesomorphic or solid-isotropic transition curve follows zig-zag path of falling and rising nature. In case of first to fifth homologues, it falls steeply and then rises for sixth homologues. Then again it leveled up to sixth homologue and again fall to the seventh homologue and falls to the twelfth member of the series with negligible rise at tenth homologue. From twelfth to fourteenth homologue the curve displays leveled up rise of very few degree of temperature. Finally it falls slightly at the last homologue. Thus, overall falling tendency is shown with the maintenance of zig-zag path in usual manner. The texture of nematic and smectic mesophases of some selected homologues are confirmed by miscibility method and other homologues are confirmed directly from microscopic observations.

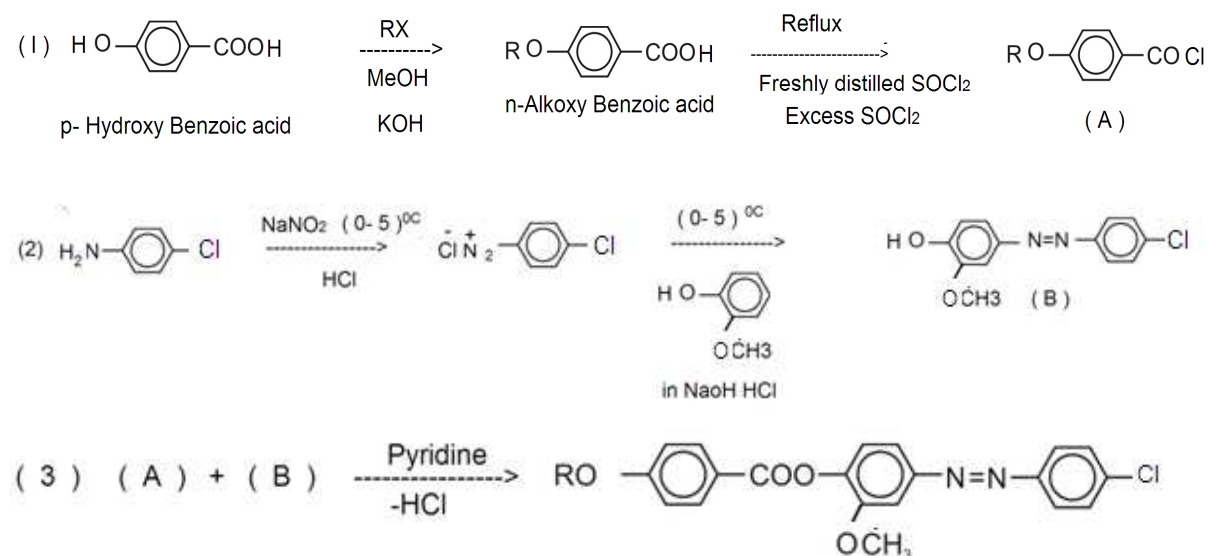
The nematic-isotropic transition curve shows Smooth descending tendency as series is ascended in usual manner. Well known odd-even effect is observed in the nematic - isotropic transition curve with alternation of transition temperatures upto seventh homologue. The smectic-nematic transition curve shows smoothly descending tendency as series is ascended with negligible rise at tenth homologue for even member of the series. Thus, smectic - nematic transition curve behaves in normal manner with odd-even effect. The series under discussion is nematogenic and smectogenic and with middle ordered melting type. The mesomorphic-isotropic transition temperatures are between 105^{0C} and 146^{0C} with mesomorphic range varying from 26^{0C} to a maximum of 64^{0C} at the fifth homologue of the series. Enantiotropic nematic property is shown from third member of the series due to proper alignment of molecules at an angle less than 90^{0C} to the plane of the surface as a consequence of anisotropic forces of intermolecular attractions of suitable magnitude pertaining molecular rigidity and flexibility. Thus, maintainance of statistically parallel orientations of molecules caused by end to end intermolecular anisotropic forces of attractions in floating condition resisting thermal vibrations. First two members of the homologues series are non-mesogenic because of their high crystallising tendency and the incapability of intermolecular cohesion forces to maintain parallel orientations or sliding layer formation of molecules in the floating condition. Early commencement of smectic mesophase in present homologous series is attributed to the less extent of non co-planarity [7] caused by the

molecules. The oxygen atom of the central carboxy group in the molecules of series (1), (A) and (B) bumps in to the nonbonded sides of the adjacent hydrogens of the aromatic ring which causes considerable strain on the molecule. Consequently a twist around C-O bond occurs, forcing the phenyl ring out of the plane of the molecule, causing reduction in extent of noncoplanarity. This effect operates equally due to laterally substituted $-\text{OCH}_3$ group in series (1) and (B), but differently operate in case of series (A) due to laterally substituted $-\text{CH}_3$ group. The another central bridge $-\text{N}=\text{N}-$ certainly endows the molecules with coplanarity in the trans position but presence of 3,4dichloro and para chloro with laterally substituted $-\text{OCH}_3$ group in series (1) and (B) as well as $-\text{Cl}$ group in para position with laterally substituted $-\text{CH}_3$ in series(A) causes difference in the reduction of extent of noncoplanarity of molecules of series (1), (A) and (B). On account of this difference, smectic mesophase commences from fourth, twelfth and fifth homologues of series (1), (A) and (B) respectively. Intermolecular forces of attractions are capable to maintain sliding layered arrangement of the molecules from and beyond forth member of the series. It is seen that nematic-isotropic and smectic-nematic transition curves show alternation of transition temperatures from third to seventh homologue resulting into emergence of odd-even effect but alternation diminished as series is ascended because higher homologues are of even membered and in case of higher homologues the longer left n-alkyl chain of n-alkoxy group may be coupled or coiled to lie in the line with major axis of the core. Thus, end to end contact would then ultimately be the same for odd and even homologue.

The average thermal stability of series (I), (A)¹⁶, (B)¹⁷, (figure-2) are given in table-3. Nematic-isotropic thermal stability of homologous series (A) and series(1) is in the decreasing order while series (B) is only Smectogenic and does not show any nematogenic character. The ratio of length to breadth of molecule and ratio of polarity to polarisability for lateral substituents varies and this variation is a direct reflection of degree of mesomorphism (smectic and / or nematic) and presence or absence of nematic and / or smectic character in case of homologous series (I) , (A) , and series (B) under comparison. The decreasing order of polarity in combination with the ratio of polarity to polarisability of lateral substituent in above sequence decreases net intermolecular attractions and therefore, nematic-isotropic thermal stabilities decreases. There are also several reports in literature¹⁸⁻¹⁹ which prove that lateral substituents depress the thermal stabilities of the compounds. Reference to table-3 indicate that smectic-nematic or isotropic-smectic thermal stability of homologous series(I) is lower then series (A) and (B).This can be attributed to difference in polarity of phenyl ring $-\text{OCH}_3$ to ring $-\text{CH}_3$.The lateral methoxy group increase the breadth (equivalent to $-\text{CH}_2-\text{CH}_3$) of the molecule more than the $-\text{CH}_3$ group, thereby reducing smectic thermal stability.

Thus, the smectic and nematic group efficiency order derived on the basis of average thermal stability in presence of $-\text{Cl}$ or dichloro end group.

Smectic group	$-\text{CH}_3$ in		$-\text{OCH}_3$ in		$-\text{OCH}_3$ in
Efficiency order	Presence of	~	presence of	>	presence of
	$-\text{Cl}$ terminal		3,4 dichloro		$-\text{Cl}$ terminal
			Terminal		

Scheme of synthesis**Figure-III****Table -1 : Transition temperatures of the homologous series 4- (4'-n-alkoxy benzoyloxy) -3- methoxy phenyl azo -4''- chlorobenzenes**

Sr.no.	R=n-alkyl gr.	Transition temperatures in °		
		Smectic	Nematic	Isotropic
1.	Methyl	—	—	165.0
2.	Ethyl	—	—	153.0
3.	Propyl	—	118.0	146.0
4.	Butyl	82.0	109.0	145.0
5.	Pentyl	72.0	89.0	136.0
6.	Hexyl	94.0	101.0	133.0
7.	Heptyl	76.0	87.0	129.0
8.	Octyl	72.0	90.0	123.0
9.	Decyl	69.0	88.0	116.0
10.	Dodecyl	61.0	78.0	114.0
11.	Tetradecyl	67.0	74.0	109.0
12.	Hexadecyl	63.0	72.0	105.0

Table -2 : Elemental analysis for 4-(4'-n-alkoxy benzoyloxy) -3- methoxy phenyl azo -4''- chlorobenzenes

Sr. No.	R=n-alkyl chain	M.F.	Found % of N	Calculated % of N
1.	Methyl	C ₂₁ H ₁₇ N ₂ O ₄ Cl	7.06	6.96
2.	Ethyl	C ₂₂ H ₁₉ N ₂ O ₄ Cl	6.82	6.78
3.	Heptyl	C ₂₇ H ₂₉ N ₂ O ₄ Cl	5.82	5.63
4.	Dodecyl	C ₃₂ H ₃₉ N ₂ O ₄ Cl	5.08	5.24

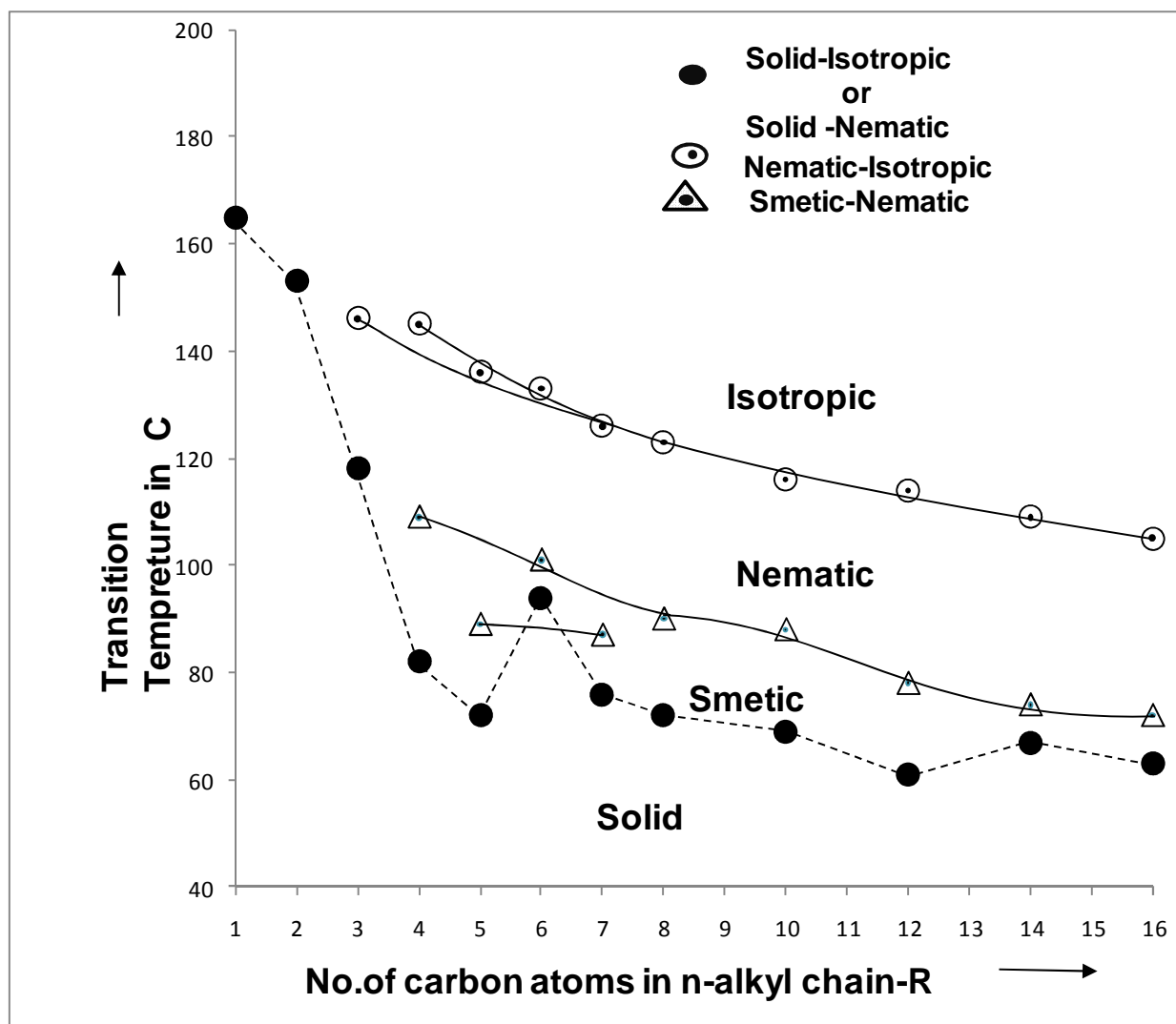


Figure-1: 4- (4'-n-alkoxy benzoyloxy) -3- methoxy phenyl azo -4'- chlorobenzenes

CONCLUSION

New mesogenic azoester homologous series with lateral methoxy group on the central phenyl ring has been synthesized. The study indicates that lateral substituents affect the mesophase thermal stabilities and the range of liquid crystallinity.

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