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Der Pharma Chemica, 2011, 3(2): 135-141

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ISSN 0975-413X  
CODEN (USA): PCHHAX

### Liquid Crystalline Characteristics of Azoester New Homologous series: p-(p'-n-alkoxy benzyloxy) phenyl azo-p''-methoxybenzene

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#### ABSTRACT

A homologous series with -COO- and -N=N-, as central groups have been synthesized by treating p-n-alkoxy benzoyl chlorides with p-methoxy -p'-hydroxy azobenzene. All the homologues of the series are mesomorphic in nature. The nematic type mesophase commences from the very first member of the series. Polymesomorphism is exhibited by tetradecyl homologue i.e. smectic and nematic mesophases appear, one after another. Hexadecyl member is purely smectogenic. On plotting transition temperatures versus number of carbon atoms in n-alkyl chain of left n-alkoxy terminal, a phase diagram is obtained. Solid-isotropic /mesomorphic transition curve, shows usual zigzag path of rising and falling. Nematic-isotropic and smectic - isotropic transition curves behave in normal manner with and without odd-even effect respectively. The series is high melting type with considerable mesomorphic range. Thermal stability and other mesogenic properties are comparable with structurally similar known series. Analytical data support the structure. Transition temperatures are determined by hot stage polarizing microscope. Texture of nematic and smectic mesophases confirmed by miscibility method. Nematic mesophase is of threaded type and that of smectic mesophase are focal conic fan shaped of type smectic-A for tetradecyl and smectic-C for hexadecyl homologue.

**Key words:** Liquid crystal, mesomorphism, nematic, smectic, Mesogens.

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#### INTRODUCTION

Number of azoester homologous series of mesogens are reported earlier with a view to understand effect of structure on mesomorphic properties of a substance and their applications in various fields like manufacture of electronic display devices ( LCD) e.g. screen of television, electronic curtains, medical field to manufacture thermo graphic articles e.g. for identification or

to locate the cancerous part of the body or in immediate operation of a pregnant lady to locate the place of magenta etc; analysis of drugs and chemicals etc. Present work is planned to synthesis, new liquid crystal material through homologous series and to determine mesomorphic range and other mesomorphic properties with structure determination by spectroscopic method.

### MATERIALS AND METHODS

- (1) p-Methoxy p'-hydroxy azobenzene was prepared by known procedure<sup>1</sup>.
- (2) Alkoxy benzoic acids were prepared by the modified method reported by Vora and Dave<sup>2</sup>.
- (3) Alkoxy benzoyl chlorides were prepared by usual established method<sup>3,4</sup> and directly condensed with p-methoxy -p'-hydroxy azobenzene in pyridine. Azoester formed are purified and recrystallized from alcohol.
- (4) Transition temperatures of homologues of the titled series were observed through leitz labourlux 12 POL microscope with heating stage.
- (5) Analytical data of some selected homologues are determined and confirms the structure of homolgues.

*Schematic diagram of synthetic route is separately represented in figure-III.*

**Table-1: Transition temperatures**



Sr.no	R= n-alkyl group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	165.0	335.0
2	Ethyl	-	169.0	326.0
3	Propyl	-	103.0	173.0
4	Butyl	-	120.0	302.0
5	Pentyl	-	108.0	262.0
6	Hexyl	-	128.0	265.0
7	Heptyl	-	120.0	252.0
8	Octyl	-	122.0	242.0
9	Decyl	-	121.0	219.0
10	Dodecyl	-	125.0	202.0
11	Tetradecyl	116.0	136.0	191.0
12	Hexadecyl	112.0	-	138.0

#### Analytical data:

#### I.R. spectra :

#### Butyl homologue;

2921,2848  $\text{cm}^{-1}$  confirm alkyl group.

1729  $\text{cm}^{-1}$  confirm  $> \text{C}=\text{O}$  ester.

1495, 1463, 1579, 1605  $\text{cm}^{-1}$  confirm aromatic phenyl ring.

1320  $\text{cm}^{-1}$  confirm  $-\text{N}=\text{N}-$

1257, 1169 $\text{cm}^{-1}$  confirm C-O ether linkage.  
844  $\text{cm}^{-1}$  confirm p- substituted phenyl ring.

### Octyl homologue;

2940,2856  $\text{cm}^{-1}$  confirm alkyl group.  
1735  $\text{cm}^{-1}$  confirm  $> \text{C}=\text{O}$  ester.  
1500, 1471, 1582, 1610  $\text{cm}^{-1}$  confirm aromatic phenyl ring.  
1322  $\text{cm}^{-1}$  confirm  $-\text{N}=\text{N}-$   
1257, 1069 $\text{cm}^{-1}$  confirm C-O ether linkage.  
849  $\text{cm}^{-1}$  confirm p- substituted phenyl ring.

**Texture of mesophase :** by miscibility method for nematic and smectic.

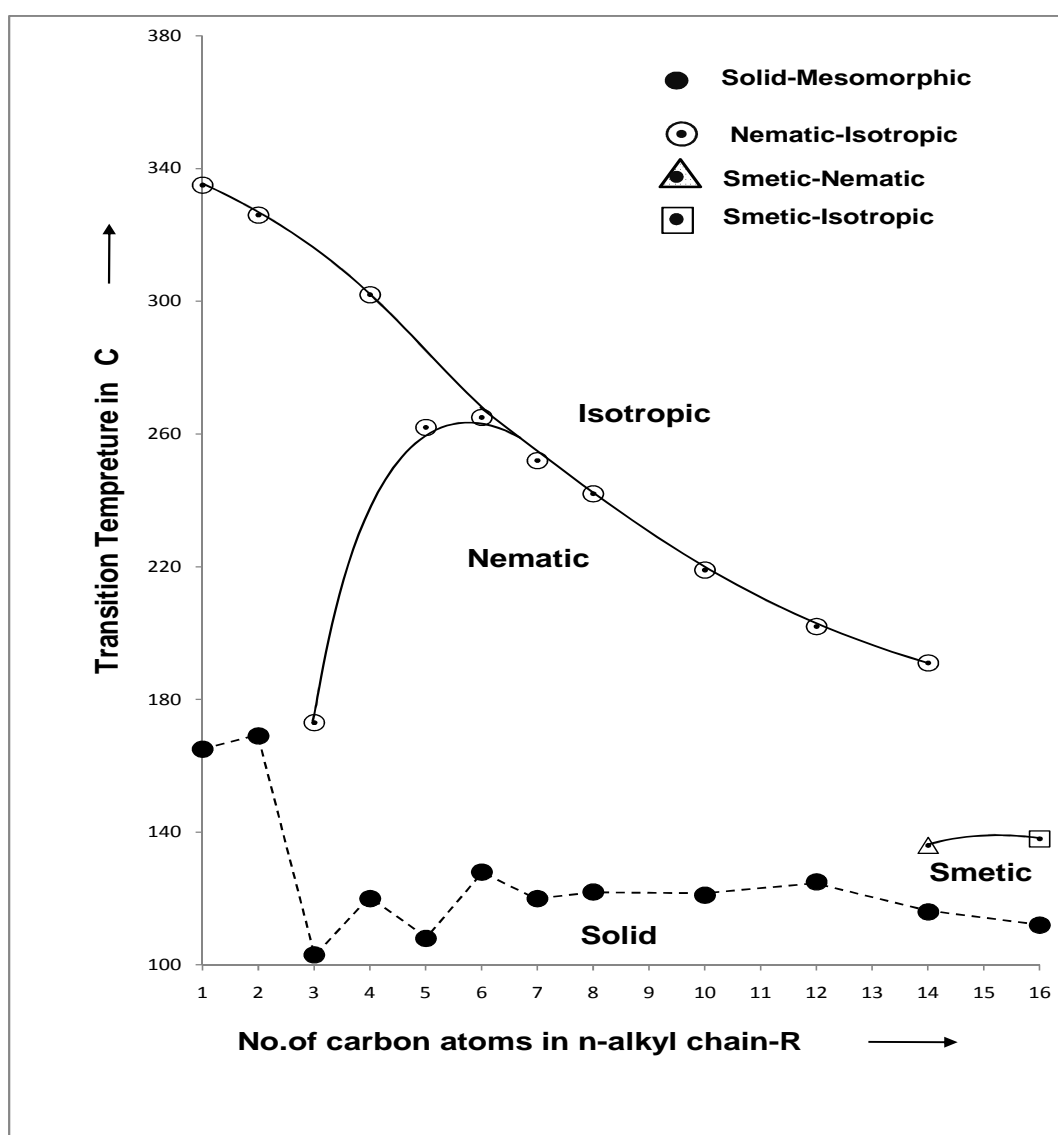


Figure :I -p- (p'-n-alkoxy benzyloxy) phenyl azo-p''-methoxybenzene

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## RESULTS AND DISCUSSION

Homologous series p-(p'-n-alkoxybenzoyloxy) phenylazo-p''- methoxybenzenes is entirely mesomorphic. The nematic type of mesophase commences from the very first member of the series. Polymesomorphism is exhibited by tetradecyl homologue. i.e. smectic and nematic mesophase appear one after another. Hexadecyl member is purely smectogenic. On plotting the transition temperatures (Table-1) versus the number of carbon atoms in n-alkyl chain of the left n-alkoxy end group, a phase diagram obtained is given in figure-I. smooth curves are drawn through points for like or related transitions.

The nematic-isotropic transition curve shows smooth descending tendency as series is ascended, a characteristic of high melting series. In case of third homologue, it assumes a lower value of the transition temperature. The solid-mesomorphic curve follows zigzag path of rising and falling nature. In case of first to seventh member of the series, it shows rise and fall of solid-nematic transition temperatures. From and beyond the seventh homologue of this series, the solid-mesomorphic curve shows an overall falling tendency with negligible rise at eighth and twelfth homologue. Nematic-isotropic transition curve behaves in a normal manner. Series is of high melting type with alternation of transition temperature in nematic-isotropic transition curve. Nematic mesophase is of threaded type of texture and smectic mesophase is of focal conic fan-shaped texture as determined by miscibility method for tetradecyl and hexadecyl homologues, which are of the type, smectic-A and smectic-C respectively.

p-Methoxy p/-hydroxy azobenzene is a non-mesomorphic azodye but on linking it with acid chlorides of dimerised n-alkoxy benzoic acids, give rise to azo-ester homologues with liquid crystal or mesomorphic properties. The dimerization of n-alkoxy benzoic acids disappear by esterification due to breaking of hydrogen bonding between two phenyl rings. The homologues formed in solid state may have layered or un-layered crystal lattices of entropy (S) or randomness or disorderness value  $\Delta H/T$ . The entropy is as low as near to zero ( depending upon temperature) according to third law of thermodynamics, where  $T=t^{0C}+273$ . T is absolute temperature in degree Kelvin and t = temperature in degree centigrade. If a sample of the substance homologue in solid state, under study is considered as a system and rest part of universe is considered as surroundings, then a system under supply of heat energy [ $\Delta H$ =enthalpy change] from surrounding acquire and absorbs heat, exposed upon molecules of a sample (system) under investigation. i.e. the molecules of a sample substance are energized. On increasing the temperature, more and more energy will be absorbed by molecules. As temperature rises, homologue molecules sequentially passes from translation motion to rotational motion and rotational motion to vibrational motion with increasing magnitude of disorder or randomness or entropy ( $\Delta S$ ) as a result of absorbing externally supplied heat energy ( $\Delta H$ ) from surrounding which fights or operates or works against intermolecular adhesion forces of attractions.

Under this situation, appearance or disappearance of mesomorphic state depend upon the, positional status of molecules to resist the thermal vibrations exposed upon them from surroundings. If the molecules of sample substance are disaligned in floating condition under the influence of exposed thermal vibrations, the homologue is nonliquid crystal or nonmesomorphic and if molecules are not disaligned in floating condition under the influence of exposed thermal

vibrations from surroundings, then, exhibition of mesomorphic or liquid crystal state, occur at a temperature  $t_1$  and continue up to higher temperature  $t_2$  i.e.  $t_2 > t_1$  for enantiotropic LC. The mesophase range or mesophase length is  $(t_2 - t_1) ^\circ\text{C}$ . In case of monotropic LC  $t_2 < t_1$ . The temperature above  $t_2$  in case of enantiotropic LC results into isotropic liquid of high degree of randomness or high order of molecular disorder and high value of entropy at which molecules are randomly oriented in all possible directions in floating condition without any regularity. Thus, mesophase formation require intermolecular anisotropic forces of attractions of suitable magnitude. Now exhibition of nematic mesophase by methyl to tetradecyl homologues is attributed to the intermolecular anisotropic forces of adhesion of suitable magnitude arising as a consequence of molecular rigidity, flexibility and molecular bending for observed nematogenic range of temperature for unlayered crystal lattices in case of methyl to dodecyl homologues and for layered crystal lattices of tetradecyl homologue. Thus, intermolecular anisotropic forces of adhesion of suitable magnitude are able to resist thermal vibrations and restricts molecules of methyl to tetradecyl homologue to disalign and to cause statically parallel orientations of molecules in floating condition at a given temperature. Therefore nematogenic mesophase appear. The appearance of smectic mesophase in tetradecyl and hexadecyl homologues is due to the presence of layered crystal lattices present inially with lamellar packing of molecules, which causes sliding layered arrangement of molecules in floating condition without any disruption of sliding layered of molecules for definite temperature range maintaining smectic mesophase formation. The mesomorphic properties of titled homologous series (1) are compared with structurally similar homologous series (A), p-(p'-n-alkoxy benzyloxy ) benzyliidene -p''-anisidine.

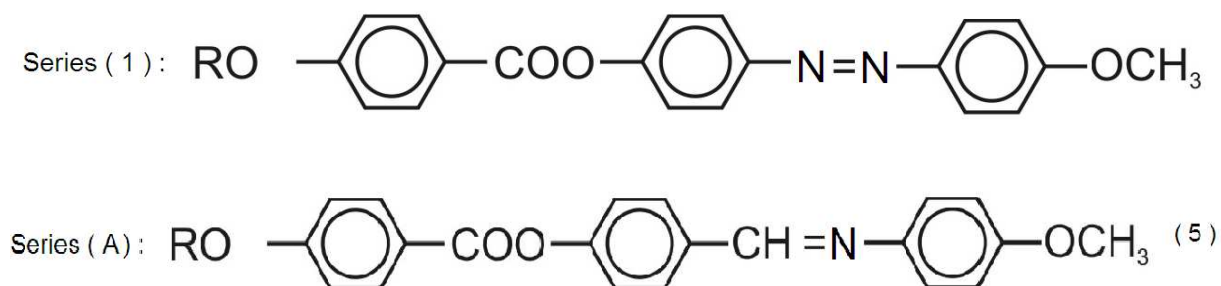


Figure -II

The molecular geometry of homologous series under comparison in resemble all respect except one of the central bridges i.e.  $-\text{N}=\text{N}-$  of series (1) is replaced by  $-\text{CH}=\text{N}-$ . Therefore comparing  $-\text{N}=\text{N}-$ , it clearly indicate that  $-\text{CH}=\text{N}-$  replace  $-\text{N}=\text{N}-$ . naturally, the overall polarity and polarizability of the molecules bonding to these homologous series under comparison will be comparable including the effect due to noncoplanar nature of the molecules. Thus, most of the mesomorphic characteristics should also be comparable. The reasons for all the variation that arise can obviously be traced to the different central bridges linking second and third phenyl ring i.e. replacement of  $-\text{N}=\text{N}-$  by  $-\text{CH}=\text{N}-$ . Table-3 shows the average thermal stabilities ( $^\circ\text{C}$ ) and the stage of commencement of the smectic phase for the homologous series under comparison.

Table -3 : Average thermal stabilities in °C

Series	Average transition temperatures in °C	
	Series (1)	Series(A)
Nematic-isotropic	251.7 (C <sub>1</sub> -C <sub>14</sub> )	246.5 (C <sub>6</sub> -C <sub>8</sub> )
Smectic-nematic or Smectic-isotropic	137.0 (C <sub>14</sub> -C <sub>16</sub> )	123.4 (C <sub>12</sub> -C <sub>16</sub> )
Commencement of smectic phase	C <sub>14</sub>	C <sub>12</sub>

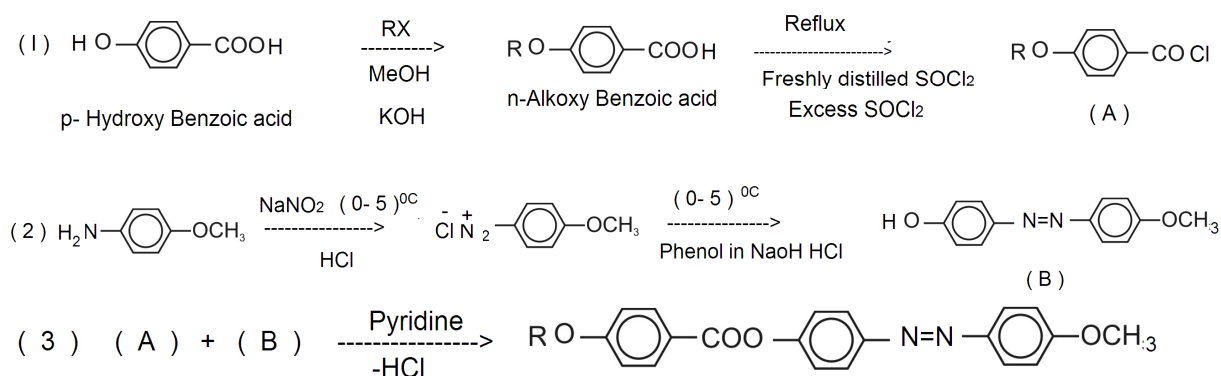
The nematic-isotropic thermal stabilities of the homologous series (1) is higher than the homologous series (A). The smectic-nematic or smectic-isotropic thermal stabilities follows similar trend. Looking to the molecular structure, the intermolecular attractions amongst molecules vary due to the parts  $-\text{CH}=\text{N}$  and  $-\text{N}=\text{N}$  of a central bridge  $-\text{CH}=\text{N}$  and  $-\text{N}=\text{N}$ - respectively. The lateral attractions amongst the molecules of series (1) and series (A) play greater role as compared to the role played by end to end attractions. A linear  $-\text{N}=\text{N}$  group having two pair of electrons and non-polar double bond while  $-\text{CH}=\text{N}$ - group is nonlinear with only one pair of electrons. Hence intermolecular lateral attractions are stronger in case of series (1) as compared to series (A). Therefore molecules of azoesters series (1) are more closely packed than the molecules of series (A). Thus, intermolecular anisotropic forces are strong enough to withstand thermal vibrations imposed by surrounding to system. Thus, thermal stabilities for smectic and nematic of series (1) are higher than series (A). The difference of thermal stabilities for smectic is more than the nematic. This is because of the relatively strongly inter linked crystal lattices of layered arrangement of molecules due to linear  $-\text{N}=\text{N}$ - group. The order for smectic and nematic group efficiency is derived on the basis of thermal stabilities is as under.

Smectic and nematic group efficiency :  $-\text{N}=\text{N}- > -\text{CH}=\text{N}-$

The commencement of smectic mesophase depend upon the extent of noncoplanarity (5) caused by a molecule. A molecule with less noncoplanarity cause early commencement of smectic mesophase.

The commencement of smectic mesophase occur at twelfth homologue in case of series (A) while, it occurs at the fourteenth homologue in series (1). This is because  $-\text{N}=\text{N}$ - group is planer and linear while  $-\text{CH}=\text{N}$ - is nonplaner and nonlinear. Therefore extent of noncoplanarity caused by molecules of series (A) should be more than series (1). However, a rod like linear molecule of series (1) undergo more twist along its major axis, while in case of series (A), though a molecule being nonlinear due to  $-\text{CH}=\text{N}$ - part, the hydrogen atom restricts the twist of a molecules as compared to a molecule of a series (1). Thus, the extent of noncoplanarity is not as expected but reduced as compared to the extent of noncoplanarity caused by a molecule of series (1). Thus, this difference of under identical condition. This difference result into early commencement of smectic mesophase in series (A).

Thus, order for early commencement of smectic mesophase is,  $-\text{CH}=\text{N}- > -\text{N}=\text{N}-$

**Scheme of synthesis:****Figure -III****CONCLUSION**

A new homologous series have been synthesized. The order for smectic and nematic group efficiency is  $-N=N-$  >  $-CH=N-$  and for early commencement of smectic mesophase is  $-N=N-$  >  $-CH=N-$  in azoester series.

**Acknowledgement**

Authors are thankful to Ex. Prof. and Head, Dr. R. A. Vora and Dr. N. D. Jadav, M. S. University, Baroda for their valuable co-operation in the work. Thanks are due to the CSMCRI, Bhavnagar for analytical services.

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