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Synthesis and Study of Thermotropic Mesogenic Homologous Series: *p*- (*p*'-*n*-alkoxy benzoxyloxy)-*m*- Chlorophenyl azo-*p*''- Chlorobenzenes

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ABSTRACT

A mesogenic homologous azoester series is synthesized with a view to understand the effect of laterally substituted functional group on mesogenic characteristics of a molecule. Titled homologous series is synthesized by reacting *p*-hydroxy- *m*-chlorophenyl azo -*p*'-chlorobenzen and corresponding acid chloride of *p*-*n*-alkoxy benzoic acid in dry pyridine by established method. Products were purified by alcohol. Mesogenic characteristics commences from its propyl derivative. Propyl to octyl derivatives are only enantiotropic nematic. Smectic property commences from decyl derivative. Decyl, dodecyl, tetradecyl, and hexadecyl derivatives exhibit both smectic and nematic mesophase in enantiotropic manner. Methyl and ethyl derivatives are non-mesogenic. Transition temperatures are observed through an optical polarising microscope with heating stage. Smectic mesophase range is relatively shorter than nematic mesophase range. Series is of middle ordered melting type. The solid-isotropic or solid-smectic (or nematic) and nematic-isotropic transition curves behave in normal manner, except with negligible abnormality in case of some members of the series. Odd-even effect is observed in nematic-isotropic curve upto heptyl/octyl derivatives. The texture of nematic mesophase is threaded type and that of smectic mesophase in case of hexadecyl derivative is of Sm-C type, while, rest of the smectogenic members exhibit smectic mesophase are of the type A as determined from miscibility method. Enthalpy (ΔH) and entropy (ΔS) of transition concept discussed qualitatively. Analytical data support the structures of molecules. Thermal stability and mesogenic characteristics are comparable with structurally similar homologous series.

Keyword: Smectic phase, Nematic phase, Liquid Crystal, Mesophase.

INTRODUCTION

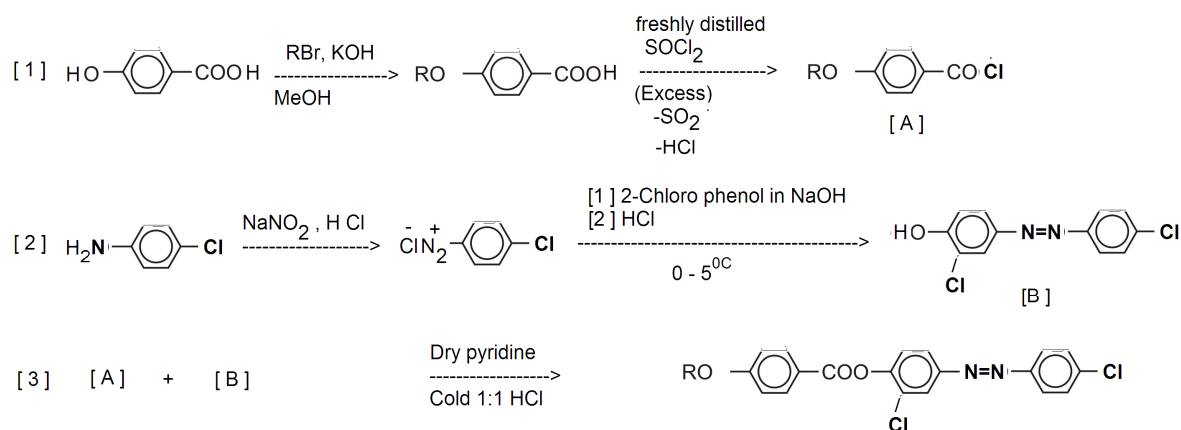
A number of homologous series with two or three phenyl rings linked through one or two central group respectively with narrow lath like molecular geometry are reported earlier [1-6]. Present work is planned with a view to synthesize new azoester homologous series of three phenyl rings

linked through two central bridges Viz. $-\text{COO}-$ and $-\text{N}=\text{N}-$ and functional group $-\text{Cl}$ substituted on middle phenyl ring at the lateral *meta* position with respect to $-\text{N}=\text{N}-$ central group. As a result of this, linearity of narrow lath like molecular geometry is disturbed and consequently mesogenic characteristics and a range of mesomorphism as well as thermal stability of a molecule may vary accordingly to lower down phase transition temperatures. Such liquid crystalline material may be useful in various fields of applications today and tomorrow. Thus, effect of structure on mesogenic characteristics can be studied by comparing structurally similar other homologous series with titled homologous series.

MATERIALS AND METHODS

All chemicals used for the synthesis were of reagent grade and the intermediates prepared as per known literature procedure. ^1H NMR spectra were recorded on Bruker spectrometer using CDCl_3 as solvent. IR spectra were recorded on perkin Elmer spectrum. Liquid crystalline properties were investigated on a Leitz Laboulux 12POL polarising microscope with a heating stage. The synthetic rout to the present series is illustrated in the **scheme-1**.

Scheme of Synthesis



Where $R = \text{C}_n\text{H}_{2n+1}$, $n = 1 \text{ to } 8, 10, 12, 14 \text{ and } 16$.

(a) *p-n*-alkoxy benzoyl chlorides were prepared by modified method of Vora and Dave [7-8].

(b) *p*-hydroxy - *m* - chlorophenyl azo-*p'*- chlorobenzene was prepared by reacting *o*-chlorophenol and *p*-chloroaniline by usual method of diazotization and coupling[9]. The azodye formed was filtered, washed with water, dried and crystallized by glacial acetic acid till it gave constant melting point (115.0°C). Yield is 68-70%.

(c) Title homologous series *p*-(*p'*-*n*-alkoxy benzoyloxy)-*m*-chlorophenyl azo-*p''*-chlorobenzenes was synthesized by condensing azodye (b) and corresponding *p-n*-alkoxy benzoyl chloride (a) in dry pyridine. Azoester formed were purified in alcohol. I.R. spectra, ^1H NMR spectra and elemental analytical data of some selected homologues determined and support the structure (table -1). Attempt is made to determine the value of enthalpy (ΔH) and entropy (ΔS) of transition from peak value of D.S.C. scan. However, due to some unavoidable difficulties of standard analytical laboratory providing analytical services, it could not be done and concept of entropy of transition discussed qualitatively.

Type of smectic-A and smectic-C are determined from miscibility method.

Table-1:Elemental analysis for p-(p'-n-alkoxy benzyloxy)-m-Chlorophenyl azo-p''-Chlorobenzenes

Sr. No.	R=n-alkyl chain	Calculated %			Observed %		
		C	H	N	C	H	N
1.	Butyl	62.30	4.51	6.32	62.39	4.63	6.49
2.	Dodecyl	67.02	6.48	5.04	66.88	6.41	5.51
3.	Tetradecyl	67.92	6.86	4.80	68.04	6.59	4.45
4.	Dodecyl	68.73	7.20	4.58	68.78	7.37	4.68

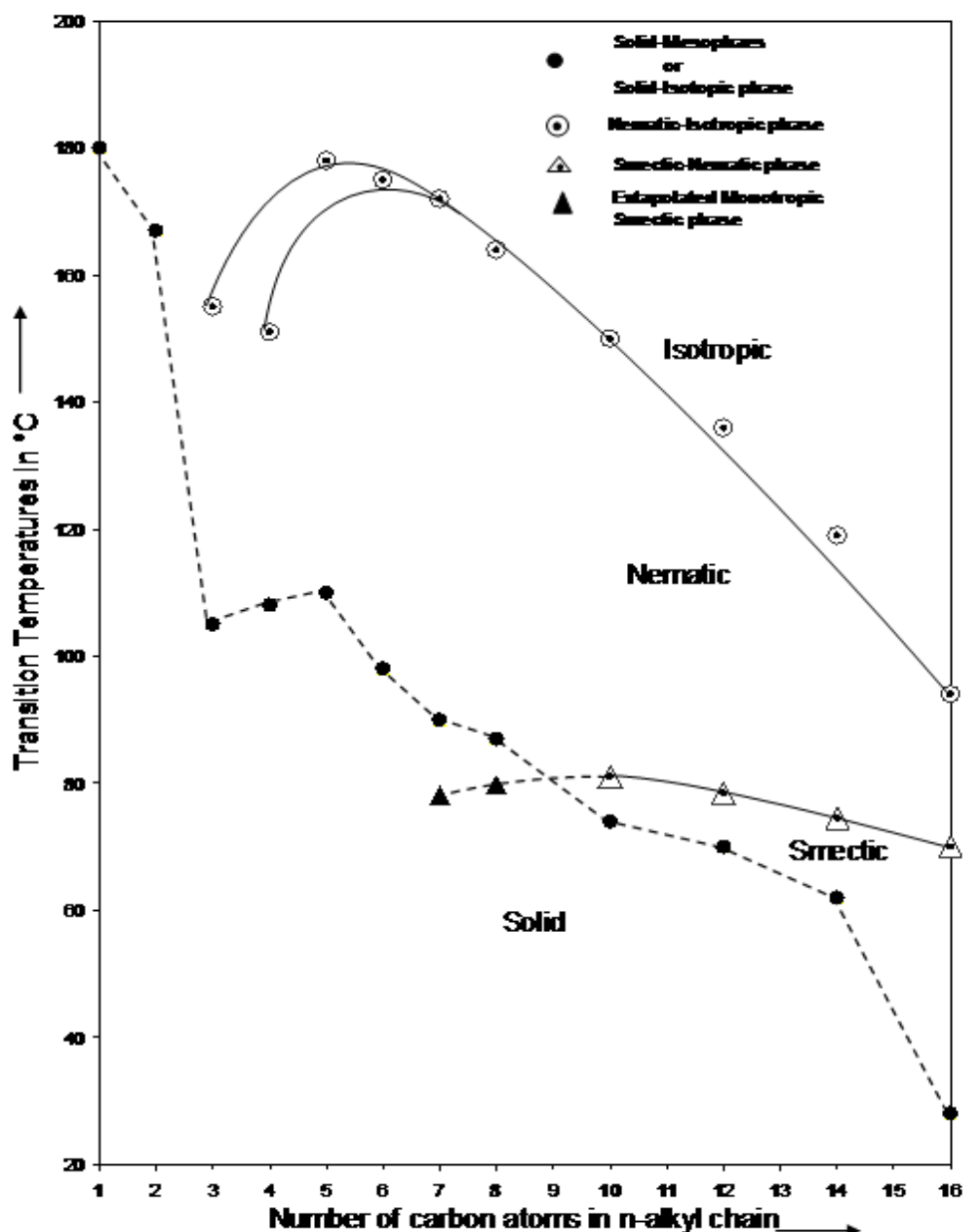


Fig: | p-(p'-n-alkoxy benzyloxy)-m-chlorophenylazo-p''-chlorobenzenes.

Table-2: Transition temperatures for p-(p'-n-alkoxy benzoyloxy)-m-Chlorophenyl azo-p''-Chlorobenzenes. Transition Temperatures

Sr.no	R= n-alkyl group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	180.0
2	Ethyl	-	-	167.0
3	Propyl	-	105.0	155.0
4	Butyl	-	108.0	151.0
5	Pentyl	-	110.0	178.0
6	Hexyl	-	98.0	175.0
7	Heptyl	-	90.0	172.0
8	Octyl	-	87.0	164.0
9	Decyl	74.0	81.0	150.0
10	Dodecyl	70.0	78.0	136.0
11	Tetradecyl	62.0	74.0	119.0
12	Hexadecyl	28.0	70.0	94.0

IR (KBr) for n-Hexyloxy derivative ($\nu_{\max}/\text{cm}^{-1}$): 3064(-C-H aromatic stre.), 2927, 2852, 1429 (alkyl group), 1726, 1255, 1166 (ester group), 1419(-N=N- group), 1579.6(-C=C-aromatic stre.), 1061(ether group), 842(p-sub. Benzene ring), 1120.6 (C-Cl aromatic).

IR (KBr) for n-Decyloxy derivative ($\nu_{\max}/\text{cm}^{-1}$): 3064(-C-H aromatic stre.), 2922, 2852, 1473 (alkyl group), 1739, 1230, 1166 (ester group), 1427(-N=N- group), 1581.4(-C=C-aromatic stre.), 1066(ether group), 839(p-sub. Benzene ring), 1118.6(C-Cl aromatic).

^1H NMR (CDCl₃, Standard TMS) for n- Heptyloxy derivative, δ_{ppm} : 0.91(t, 3H,-CH₃), 1.33(m, 2H, -OCH₂-CH₂-), 4.06(t, 2H, -OCH₂-), 6.9-8.21(m, 11H, Ar-H).

^1H NMR (CDCl₃, Standard TMS) for n- Octyloxy derivative, δ_{ppm} : 1.0(t, 3H,-CH₃), 1.52(m, 2H, -OCH₂-CH₂-), 4.05(t, 2H, -OCH₂-), 6.98-8.22(m, 11H, Ar-H).

RESULTS AND DISCUSSION

Azo dye p-hydroxy-m-chloro phenyl azo-p'-chlorobenzen is nonmesomorphic in character. However mesomorphism is induced by linking of phenyl ring bridged through carboxylate central unit with p-substituted n-alkoxy terminal group. Thus presently reported azoester homologous series: p-(p'-n-alkoxy benzoyloxy)-m-chlorophenyl azo-p''-chlorobenzenes is mesomorphic in nature. Methyl and ethyl derivatives are nonmesomorphic in character. Mesomorphism commences from propyl derivative of the series. Thus, propyl, butyl, pentyl, hexyl, heptyl and octyl derivatives of the series are only enantiotropic nematogenic while decyl, dodecyl, tetradecyl and hexadecyl derivatives do exhibit both, nematic[10] and smectic mesophase within definite range of temperature enantiotropically. Smectic-nematic transition curve is extrapolated for heptyl and octyl derivatives in phase diagram; which give hypothetical values of predicted latent monotropic transition temperature 87°C and 88°C respectively i.e. heptyl and octyl derivatives are actually not smectogenic but may display monotropic smectic character if proper ideal condition of rate of cooling maintained. Thus, predicted latent transition temperatures of the heptyl and octyl derivatives can be determined and confirmed by study of

their binary mixtures with suitably selected second component. Thus, homologous series under discussion is partly smectogenic in combination with predominant nematogenic character. Transition temperatures are plotted versus the number of carbon atoms in *n*-alkyl chain of left *n*-alkoxy group (Figure-I) from the table-2. Smooth curves are drawn through the like or related points of transition as shown in Figure-I. From the phase diagram obtained (Fig.-I), it is seen that, solid-isotropic or solid-mesomorphic transition curve follows zig-zag path with overall falling tendency in normal manner except in case of butyl and pentyl derivatives in which rise of about ten to twelve degree persisted. Smectic – nematic transition curve behaves in normal manner without showing up odd-even effect. Nematic – isotropic transition curve initially rises and gradually falls with exhibition of odd-even effect in usual manner upto heptyl/octyl derivatives. The odd-even effect in nematic – isotropic curve commences from propyl derivative and merges into each other between points of curve for heptyl/octyl derivative of the series with alternation of transition temperatures. The texture of the nematic mesophase is of threaded type and that of smectic mesophase is of the type smectic-A or smectic-C. Hexadecyl derivative is of Sm-C and rest of the smectogenic homologues are of Sm-A as determined by miscibility method.

Mesogenic property exhibited by a molecule depends upon the net resultant intermolecular anisotropic forces of attraction of suitable magnitude due to its molecular shape size, linearity, polarity and polarisability, aromaticity, length to breadth ratio, type of lateral and terminal substitution, molecular rigidity and flexibility, and several other factors conducive to mesomorphism. Azo dye *p*-hydroxy-*m*-chloro phenyl azo-*p'*-chlorobenzene is nonmesomorphic and passes into isotropic liquid at its melting point. However addition of phenyl ring linked through –COO- central bridge and *para* substituted *n*-alkoxy left terminal group which increases its length, aromaticity and other related factors generating cohesive forces conducive to mesomorphism by anisotropic intermolecular forces of attractions of suitable magnitude from propyl to hexadecyl derivatives of a series under discussion. Methyl and ethyl derivatives are non-mesomorphic and melt sharply at their melting point without passing through an intermediate state, called mesomorphic state due to their high crystallizing tendency. High crystallising tendency of the molecules arises from stronger intermolecular forces of attractions, which release energy (ΔH) from system (Formation of homologue molecule) to surrounding (part of universe, other than a system). Thus, release of energy from system to surrounding causes to stability formation of homologue molecule to thermodynamically stable solid crystalline state consisting of several interlinked crystal lattices, if it is an ideal crystal. Then according to third law of thermodynamics, “the entropy (ΔS) of perfectly crystalline substance is zero at absolute zero [0°K or -273.0°C]”. Thus, molecules of homologues in solid crystalline state will have some low value of entropy (ΔS) or randomness near to zero degree $^{\circ}\text{K}$. Now on heating the solid crystalline homologue, the heat energy supplied (ΔH) (from surrounding to system) will work against intermolecular forces of attractions to break down crystal structure till crystal lattices rupture. As temperature increases, molecules of a crystalline homologue tend to pass from thermodynamically stabilized state to destabilize state of existence. Thus, molecules of substance acquire motions sequentially from translational motion to rotational motion and from rotational motion to vibrational motion with rise of temperature. Hence molecular randomness or entropy (ΔS) or disorderness of system increases with increase of temperature. Now the molecules of methyl and ethyl homologues are unable to resist thermal vibrations exposed upon them from surrounding to system (sample homologue) as consequence of its molecular rigidity in combination with molecule flexing and bending, responsible to creat

intermolecular forces of attraction which are neither anisotropic, nor of suitable magnitude which causes to undergo disalignment of molecules and high order of molecular disorder or randomness. Thus, randomly oriented disaligned molecules prevent, statistically parallel orientational order of molecules of methyl and ethyl homologues causing transformation of solid structured or unstructured samples of substance, directly into isotropic liquid of high levelled entropy (ΔS) or randomness at a given temperature [melting point] without passing through an intermediate state of existence called liquid crystal or mesogenic state. Propyl to octyl homologues are only nematogenic and decyl to hexadecyl homologues are polymesomorphic, i.e. smectic and nematic mesophases occurred one after another by decyl to hexadecyl homologues. The intermolecular forces of attractions exhibited by propyl to hexadecyl homologues are able to resist the thermal vibrations exposed upon the molecules of a sample homologue against the intermolecular forces of end to end and lateral attractions which are anisotropic and of suitable magnitude, do not allow the molecules to disalign. As a result of this, statistically parallel orientational order of two dimensional array of molecules maintained in floating condition. Moreover in case of decyl to hexadecyl homologues, sliding layered arrangement of molecules which occur in floating condition as a consequence of lamellar packing of molecules in their crystal lattices. Thus, two dimensional array of molecules of higher order in floating condition is maintained. Hence, propyl to octyl homologues are only nematogenic while, decyl to hexadecyl homologues are smectogenic in addition to nematogenic character exhibition. The texture of the nematic mesophase is of threaded type and of smectic mesophase from decyl, dodecyl and tetradecyl homologues are of the type smectic-A, as determined by miscibility method and that of hexadecyl homologue is of the smectic-C, as judged directly by visualising sample from field of view of polarizing microscope. Thus, azoester homologous series under discussion is predominantly nematogenic and partly smectogenic. The nematic – isotropic transition temperatures of an azoester homologous series under present investigation are between 94.0°C and 178.0°C with mesomorphic range varying minimum from 43.0°C at butyl derivative to a maximum of 82.0°C at the heptyl derivative of the series. Hence, series is considered as middle ordered melting type with exhibition of moderately long range of mesomorphism. Thus, liquid crystals of moderate chain length yield only nematogenic homologues [11-12] is well supported by present investigation. Odd-even effect and alternation of transition temperature observed in nematic–isotropic transition curve is attributed to the gradual sequential addition of the methylene unit through oxygen atom in left *n*-alkoxy terminal. This effect diminished as series is ascended from and beyond heptyl and octyl derivative of the series because longer *n*-alkyl chains may bend and coil without their any contribution to odd-even effect. Therefore, homologues from octyl to hexadecyl derivatives follow the normal trend of nematic-isotropic transition curve.

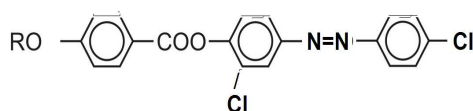
Three phenyl rings linked through –COO- and –N=N- bridges and terminally substituted –Cl group are commonly present in all the homologous series under comparison (15,16). Therefore, the over all polarity, polarisability, aromaticity, π -electron density etc. related to intermolecular forces of attraction due to above moiety operate in equal manner. Hence mesomorphic character and degree of mesomorphism for same series vary from homologue to homologue with varying *n*-alkyl chain length of left *n*-alkoxy group and changing, laterally substituted group at the middle phenyl ring, keeping terminal end group unchanged. The variation in mesomorphic properties for same homologue from series to series arises due to changing laterally substituted group at the middle phenyl ring keeping other molecular moiety unchanged.

The characteristics of present homologous series (I) is compared with other structurally similar homologous series (A) and (B) (figure-II) for their molecular characteristics and thermal stabilities and stage of commencement of mesophase as shown in Table – 3.

Table -3: Average thermal stabilities in °C

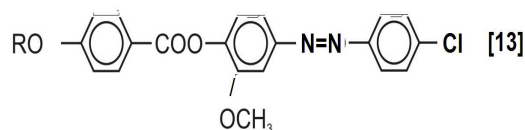
series	Series (I)	Series(A)	Series(B)
Nematic-isotropic or Isotropic-nematic	149.4 (C ₃ -C ₁₆)	125.6 (C ₃ -C ₁₆)	217.6 (C ₁ -C ₁₆)
Commencement of Nematic phase	C ₃	C ₃	C ₁
Smectic-isotropic or Isotropic-smectic	75.75 (C ₁₀ -C ₁₆)	87.55 (C ₄ -C ₁₆)	148.7 (C ₆ -C ₁₆)
Commencement of Smectic phase	C ₁₀	C ₄	C ₆

Series [I] :



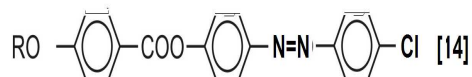
p-(p'-n-alkoxy benzoyloxy)-m-chlorophenyl azo-p''-chlorobenzenes.

Series [A] :



p-(p'-n-alkoxy benzoyloxy)-m-methoxy phenyl azo-p''-chlorobenzenes

Series [B]:



p-(p'-n-alkoxy benzoyloxy)-phenyl azo-p''-chlorobenzenes.

Figure-II

The molecular geometry of homologous series (1), (A) [13] and (B) [14] under comparison from the point of view of their mesogenic characteristics must resemble each other due to common identical molecular features. Thus, it varies among the molecules of same homologue from series to series due to the presence of uncommon laterally substituted functional group -Cl, -OCH₃ and -H in series (1), (A) and (B) respectively. Though laterally substituted group Viz. -Cl, -OCH₃ and -H are occupied at the identical position with middle phenyl ring but because of their variation in polarity, polarisability, molecular length to breadth ratio and nonco-planarity caused by the molecules by steric interactions molecular rigidity and flexibility etc. differ. Also differences cause variation in overall resultant net intermolecular anisotropic forces of attraction. Hence thermal stability, transition temperatures, mesomorphic property, degree of mesomorphism and commencement of smectic mesophase etc. show variation. Presence of -Cl, and -OCH₃ group at the meta position with respect to -N=N- central bridge increases the width

of the molecules of the series under comparison. Thus, broadening of molecules increases different magnitudes of intermolecular distance causing difference in molecular polarisability. As a result of this, intermolecular forces of attractions decreases due to increase in the intermolecular distance i.e. due to lateral substitution and at the same time anisotropic intermolecular forces of attractions increases with increase of molecular polarisability. Thus, two opposing effects operate at a time. Therefore, observed net resultant effect is a net result of the predominating effect out of two opposing effects. This net result of two opposing effects is directly related to average thermal stability and degree of mesomorphism.

It is observed from table-3 of comparative values of average thermal stability for homologous series (B), which is the highest for smectic and nematic mesophase as compared to series (1) and (A). This is happened because, molecules of the homologues of series (B) are narrow lath like without any lateral substitution at ortho or meta position (i.e. -H), while molecules of the homologues of series (1) and (A) do possess lateral substitution at meta position with respect to -N=N- central group by -Cl and -OCH₃ respectively. Thus, molecules of homologues of series (B) are relatively closely packed as compared to the molecules of series (1) and (A); due to end to end intermolecular adhesion. Average thermal stability for nematic mesophase of series (1) is higher than series (A), while for smectic mesophase, it is lower than series (A). In both the cases i.e. series (1) and (A), the molecular breadth is increased by the presence of *meta* substituted -Cl and -OCH₃ groups of varying polarity as compared to -H (series-B) respectively. Thus, considerable reduction of thermal stability of series (1) and (A) are observed as compared to series (B). Therefore, Gray's[11] view that, increase in the breadth of molecules reduces both nematic and smectic thermal stability is very well supported by present investigation. *Meta* substituted -Cl is monoatomic and relatively less polar than -OCH₃. Therefore, steric hindrance caused by highly polarizable -OCH₃ group will be more than monoatomic -Cl group. Thus, degree of nonco-planarity caused by molecules of series (1) will differ from molecules of series (A) contributing to the net adhering intermolecular anisotropic forces of attractions. Thus, nematic mesophase stabilizes more at the cost of smectic mesophase in series (1), while smectic mesophase stabilizes more than nematic mesophase in series (A) due to presence of more polar laterally substituted group -OCH₃ as compared to less polar -Cl group.

Thus, early or late commencement of smectic mesophase depends upon the extent of nonco-planarity caused by the molecule. Hence, early commencement of smectic mesophase at the cost of nematic mesophase is observed in case of series (A) and (B) as compared to series (1) from fourth and sixth homologues respectively.

Thus, from the above discussion, nematic and smectic group efficiency order derived is as under, on the basis of the thermal stability.

Nematic group efficiency order for lateral substitution: -H > -Cl > -OCH₃

Smectic group efficiency order for lateral substitution: -H > -OCH₃ > -Cl

CONCLUSION

New homologous azoester series entitled p-(p'-*n*-alkoxy benzoyloxy)-*m*-Chlorophenyl azo-p''-Chlorobenzenes is predominantly nematogenic and partly smectogenic. Lateral substitution reduces average thermal stability and transition temperatures. Hexadecyl homologue of the series

exhibits smectic mesophase from 28°C to 70°C., which may be useful for devices to be operated at room temperature or upto 70°C. Thus, credibility of the Gray's [17] view is raised by present investigation.

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