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Study of new homolgous series of Azoester Mesogens:p- (p'-n-alkoxybenzoyloxy)-m-methylphenylazo-p''-methoxybenzenes

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ABSTRACT

A new homologous series of azoester mesogens: p-(p'-n-alkoxybenzoyloxy)-m-meyhylphenylazo-p''-methoxybenzenes has been synthesized with a view to understand the relation between liquid crysral properties and molecular structure. Transition temperatures of the members of the homologous series are observed under Leits Labourlux 12 POL-polarizing microscope with heating stage. The homologues of the series show variation in textures and transition temperatures. Mesomorphism commences from the very first homologue of the series. All the members of the series exhibit enantiotropic mesomorphism except third member which exhibit monotropic-nematic behavior. Smectic mesophase commences from the dodecyl homologue of the series. Dodecyl homologue of the series exhibit polymesomorphism i.e. smectic and nematic phase are present, one after another. The series is of high melting type with considerable mesomorphic range. The thermal stabilities and mesomorphic properties of the series have been compared with other structurally similar homologous series. Texture of the nematic mesophase is of threaded type and that of smectic mesophase is, focal conic fan shaped of type- A for dodecyl and tetradecyl homologue and smectic-C for hexadecyl homologue as determined by miscibility method. Analytical data support the structure of molecules.

Key words: Liquid crystals, Nematic, Smectic, Mesogen, Mesophase.

INTRODUCTION

Liquid crystalline state of matter is exploited in various fields of applications. Naturally the molecular design conducive to liquid crystalline formation is planned for present investigation by selecting methoxy as fixed terminal group with varying n-alkoxy group along with methyl group as lateral substitution.

MATERIALS AND METHODS

Experimental:

a) p-methoxy-m'-methyl-p'-hydroxy azobenzene was prepared by known Procedure[1]
b) Alkoxy benzoic acids were prepared by the method reported by Vora and Dave[2]
c) Alkoxybenzoyl chlorides were prepared by usual established method[3,4] and directly condensed with p-methoxy-m'-methyl-p'-hydroxy azobenzene in pyridine. Azoesters formed are purified and recrystallized from alcohol.

Schematic route of synthesis is shown separately in figure-III

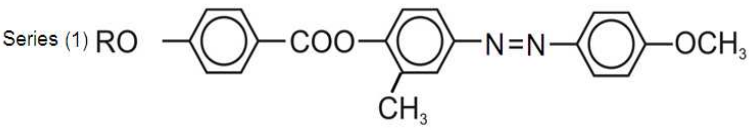
The transition temperature, elemental analysis and spectral data are recorded separately as analytical data. Enthalpy (ΔH) and entropy (ΔS) change are discussed qualitatively. Textures of homologues determine by miscibility method.

RESULTS AND DISCUSSION

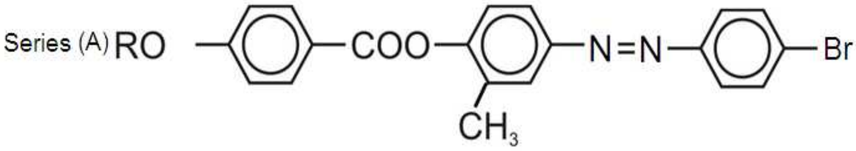
Azodye, p-methoxy-m'-methyl-p'-hydroxy azobenzene is a nonmesomorphic in character. However mesomorphic property is induced and new azoesters are formed with mesogenic character. The transition temperature as recorded in table-1 are plotted versus the number of carbon atoms in n-alkly chain of n-alkoxy terminal. Smooth curves are drawn through like points. The phase diagram obtained is, as shown in figure-I, from table-1. Dimerisation of p-n-Alkoxy benzoic acids disappeared by esterification by breaking of hydrogen bonding between two phenyl rings. Careful examination of a phase diagram reveals that, the solid mesomorphic or solid-isotropic transition curve falls in descending manner except fourth homologue which shows slight rise in temperature and fall continue up to heptyl homologue and then again rises from and beyond octyl homologue to tetradecyl homologue and finally falls to hexadecyl homologue in overall normal descending manner. Nematic-isotropic (or isotropic-nemetic) transition temperatures show odd-even effects with alternation of transition temperature.The curve falls for even numbered homologues as series is ascended in a normal manner, while it rises in case of odd members(third to seventh homologue) and finally merges into nematic-isotropic curve for even members. Smetic-isotropic transition curve behave in a normal manner. Titled homologous series does possess isotropic temperature between 105$^{\circ C}$ and 258$^{\circ C}$. Therefore series is of high melting type with considerable mesomorphic range. The nematic mesophase is of threaded type textured while smetic mesophase is of focal conic fan shapped smetic A as determined by miscibility method. Smetic-C variety of hexadecyl homologue is judged directly from the visualization of the field of view in the polarizing microscope.

The melting and transition temperature of homologues of the titled homologous series or any other substance is related with magnitude of intermolecular lateral and terminal attractive cohesive forces. Such forces are stored in the molecules depending upon the amount of energy released from a system (Birth of homologue) to surrounding (rest part of universe other than a system). Therefore give and take of energy (ΔH) or else taking place between a thermodynamic system and the surroundings. Therefore amount of energy a released from system to surrounding by a homologue correspond to magnitude of intermolecular attractions or cohesion forces and hence to the strength of layered or non layered thermodynamically stable crystalline solid homologue formed. Now on supplying heat (ΔH) from surrounding to system, a thermodynamically stable crystal interlinked crystal lattices of solid crystals will start to destabilize and tend to move from stabilized state to destabilize higher state of existence of more entropy (ΔS) or more randomness. As temperature increases by externally supplied heat energy (ΔH) from surrounding to system (homologue) the molecules of a homologue under investigation going on absorbing applied heat energy and sequentially passes from translational motion to rotational motion and from rotational motion to vibrational motion and so on, under the influence of rising temperature. If the bulk of molecules under examination can resist the thermal vibration (ΔH) exposed upon them, maintaining molecular alignment under the influences of anisotropic intermolecular forces of attractions of suitable magnitude due to their molecular rigidity and flexibility, the mesophase will form an occur, and continue for definite range of temperature. But as soon as molecules of a sample substance become unable to resist thermal vibrations (ΔH) exposed upon them to maintain molecular alignment i.e. molecules are disaligned due to absence of anisotropic intermolecular forces of attractions of unsuitable magnitude which restricts or inhibits formation of masoganic state of a substance under examination, resulting into passing directly a layered or nonlaryed solid crystalline state to isotropic liquid state without passing trough mesogenic anisotropic state of existence of higher entropy (ΔS) in which molecules are randomly oriented without any ordered arrangement of molecules. Thus, formation of liquid crystalline and nonliquid crystalline state depend upon molecular alignment and disalignment respectively. The occurrence of nematic mesophase in layered or unlayered solid crystals from methyl homologue to dodecyl homologue is attributed to the intermolecular anisotropic forces of attractions of suitable magnitude to cause statically parallel orientational order of molecules floating under aligned manner. Thus, formation of nematic mesophase take place between definite range of temperature. As soon as aligned molecules are disalin at particular temperature [T], the molecules remain individually lath like linear but, randomly orient in all possible directions in irregular manner without maintaining two dimentional array of molecules in floating condition of high order of disorder or randomness or entropy (ΔS=ΔH /T) where T is absolute transition temperature in degree Kelvin ($^{\circ}$K) i.e. T=[t + 273] where t is the temperature in degree centigrade [$^{\circ}$C]. The nematic mesophase disappears from and beyond temperature t$^{\circ C}$ under which molecules disalings in floating condition and converted to isotropic liquid. The exhibition of smectogenic mesophase in dodecyl, tetradecyl and hexadecyl homologues are attributed to the lamellar packing of molecules interlinked as crystal lattices, which on heating maintains two dimensional array of sliding layered arrangement of molecules in floating condition. The smectic mesophase disappear and nematic mesophase appear in case of dodecyl homologue at higher temperature by breaking of sliding layers and converted into aligned molecular arrangement to cause statistically parallel orientations of molecules in floating condition of ordered two dimensional array. Occurance of only smectogenic mesophase in tetradecyl and hexadecyl homologue take place by breaking of sliding layers of layered crystal lattices into disaligned molecules of high ordered, disorder or randomness or high entropy and converted directly into isotropic liquid. The odd-even effect observed in nematic-isotropic transition curve is due to the sequentially added methylene unit in left n-alkyl chain of alkoxy terminal end group affecting molecular length and flexibility of molecule. Longer n-alkyl chain may coil or couple to lie in the line with major axis of core. Thus, end to end contacts would then ultimately be the same for odd and even homologues. Laterally substituted methyl group though increases intermolecular distance and decreasing intermolecular end to end attractions, but on the other hand, this effect increases molecular polarizibility and increases intermolecular lateral attractions. These two opposing effects operate at a same time. Resulting net effect depend upon predominating effect out of two opposing effects, operating at a time.

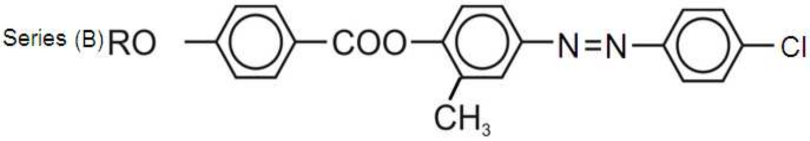
The present homologous series (1) is compared with other structurally similar series (A) [5] and (B) [5] for their molecular characteristics and thermal stabilities as given in table-4.



p-(p'-n-alkoxybenzoyloxy)-m-methylphenylazo-p''-methoxybenzenes



p-(p'¨n-alkoxybenzoyloxy) –m-methylphenylazo-p''-bromobenzenes



p-(p'-n-alkoxybenzoyloxy) –m-methylphenylazo-p''-chlorobenzenes

Figure-II

The homologous series (1), (A), and (B) possess three phenyl rings linked through carboxylate and azo central bridges, and laterally substituted methyl group at the ortho position to carboxylate central unit as common identical part. They differ with respect to the uncommon part of the molecule i.e. right side terminal end groups viz; $-OCH_3$, -Br and -Cl respectively, from series to series and left n-alkoxy terminal end group from homologue to homologue in same series. Therefore the variation in the mesomorphic characteristics and degree of mesomorphism are varied due to the variation in left and right terminal end groups. The substitution of $–CH_3$ functional group at ortho position to the carboxylate unit does not change the length of molecule but it increases the molecular width in unusual manner. Therefore length to breadth ratio and the ratio of the polarity to polarizability depends only upon the size and steric effect of the terminal end groups. The steric hindrance caused by $-CH_3$ group at ortho position to the -COO- central bridge can also equally contribute to the intermolecular packing and consequently to the degree of mesomorphism. Hence the change in bond polarity i.e. $C-O-CH_3$, C-Br, and C-Cl play an [where carbon atom belong to phenyl ring] important role on degree of intermolecular forces of attractions. This variation has direct effect on thermal stability and other liquid crystal properties.

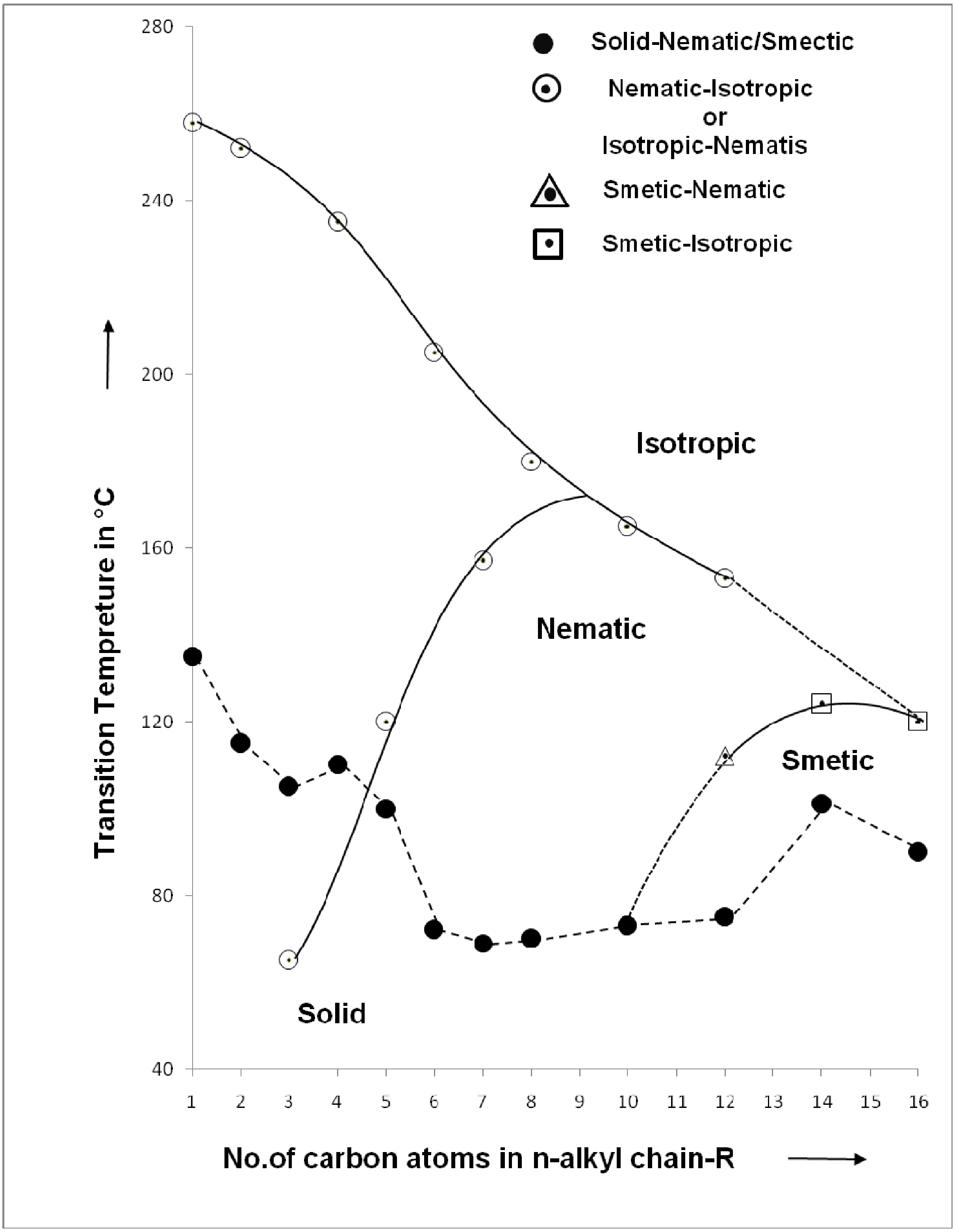
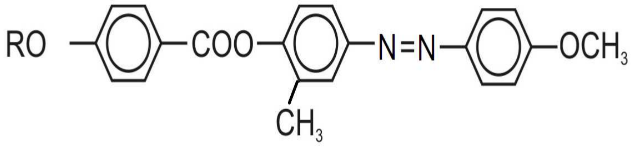


Figure –I Homologous series : - p(p'-n-alkoxybenzoyloxy)-m-methylphenyl azo-p''-methoxybenzenes

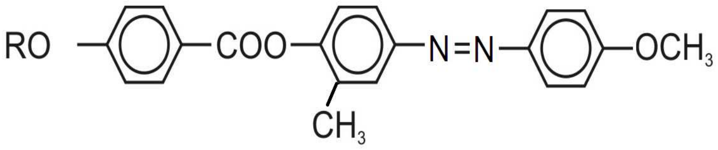
Table -1: Transition temperatures



Sr.No.	R= n-alkyl group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	135.0	258.0
2	Ethyl	-	115.0	252.0
3	Propyl	-	(65.0)*	105.0
4	Butyl	-	110.0	235.0
5	Pentyl	-	100.0	120.0
6	Hexyl	-	72.0	205.0
7	Heptyl	-	69.0	157.0
8	Octyl	-	70.0	180.0
9	Decyl	-	73.0	165.0
10	Dodecyl	75.0	112.0	153.0
11	Tetradecyl	101.0	-	124.0
12	Hexadecyl	90.0	-	120.0

( ) Indicate Monotropy*

Table-2: Elemental analysis



Sr.No.	**R=n-alkyl chain**	**Calculated %**			**Observed %**		
		C	**H**	**N**	**C**	**H**	**N**
1	Ethyl	70.76	5.64	7.17	70.68	5.57	7.11
2	Propyl	71.28	5.94	6.93	71.10	5.80	6.87
3	Heptyl	73.04	6.95	6.08	73.01	6.87	6.11
4	Decyl	74.10	7.56	5.57	74.02	7.51	5.40
5	Dodecyl	74.71	7.92	5.28	74.63	7.83	5.21

IR spectra in cm^{-1}: (R = Butyl)

2920, 2850 cm^{-1} Confirms alkyl group
1249, 1166, cm^{-1} Confirms -COO- group
1726 cm^{-1}Confirms >C=O of ester group
846 cm^{-1} Confirms p-sub. phenyl ring
1602,1581,1494,1460 cm^{-1} Confirms aromatic ring
1339 cm^{-1} Confirms -N=N-
1247, 1068, cm^{-1} Confirms -CO group

IR confirms above structure

Table-3: Average thermal stabilities

Series	(1)	(A)	(B)
Smectic – isotropic or Smectic nematic	118.6 $(C_{12} - C_{16})$	135.0 $(C_{10} – C_{16})$	106.6 $(C_{12}\text{-}C_{16})$
Commencement of smectic phase	C_{12}	C_{10}	C_{12}
Nematic – Isotropic or isotropic-nematic	183.0 $(C_1 – C_{12})$	186.7 $(C_1 – C_{10})$	161.5 $(C_1\text{-}C_{16})$
Commencement of Smectic phase	C_1	C_1	C_1

Scheme of synthesis

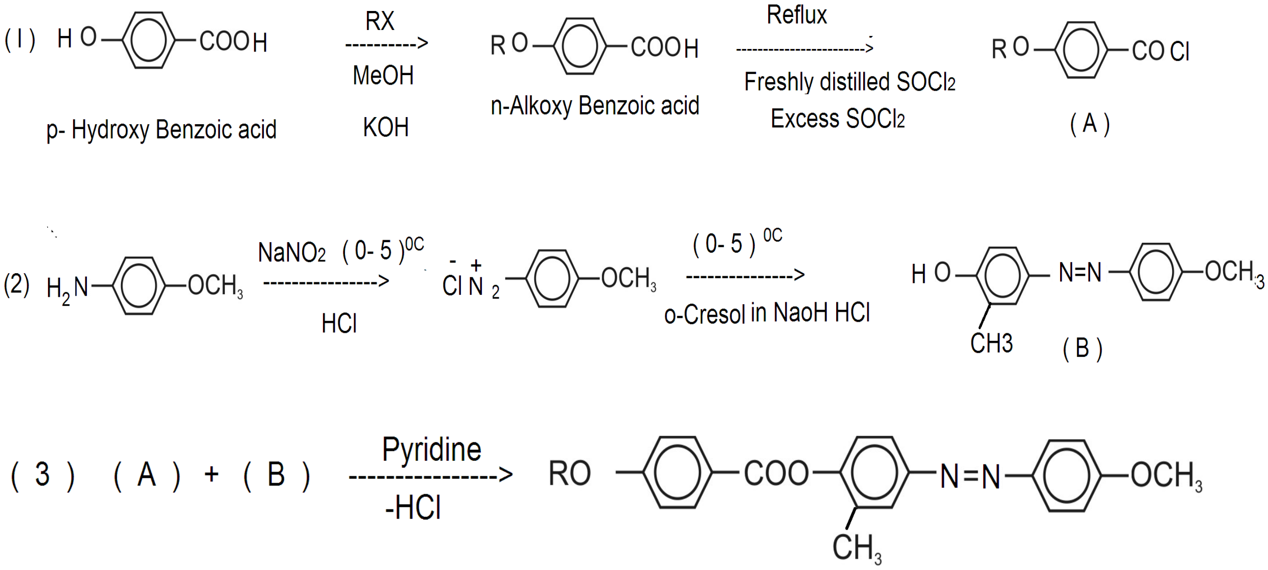


Figure-III

From table-4 it is observed that, the average thermal stabilities for smectic and nematic increases for series (1) to (A) and decreases to series (B). These suggests that the intermolecular forces of attractions amongst the molecules of the series (A) are stronger than series (1) and series (B). Presences of $-CH_3$ group increases polarizability and molecular dipolarity, resulting into strengthening of the intermolecular adhesion as series is ascended from series (1) to (A), while, it plays opposite role from series (A) to (B), in which the net intermolecular forces of attractions are weakened due to the change of predominating effect operating at a time from two opposing effects i.e. intermolecular distance i.e. polarizability predominates in case of series (B) while intermolecular packing predominates and contribute to net lateral molecular forces of attractions in case of series (1) and series(A). Thus thermal stabilities (both smectic and nematic) of series(1) is lower than series (A) and higher than series (B). The commencement of the smectic mesophase early or lates is related with the extent of non-coplanarity of the molecule. Early commencement of the smectic phase is related with less non-coplanarity of the molecules. The non-coplanarity caused by the laterally substituted $-CH_3$ group is being equally affected in all the homologous series (1), (A) and (B) under discussion, it will entirely depend upon the non-coplanarity caused by right terminal viz; -OCH_3, -Br and -Cl. The commencement of the smectic phase occurs at the twelfth homologue in case of series (1) and (B) while it commences at the tenth homologue in case of series (A). This suggests that -Br terminal create less non-coplanarity as compared to -OCH_3 and -Cl terminals. -Br and -Cl are monoatomic while -OCH_3 is nonlinear and polyatomic. But -OCH_3 is highly polarizable then -Cl and -Br. Thus, contribute to the planarity facter and molecular rigidity and flexibility.

Thus, order for early commencement of mesophase is as under:

-Br > -OCH_3 = -Cl for smectic and –OCH_3= -Br = -Cl for nematic.

The smectic and nematic group efficiency order derived on the basis of average thermal stability. When -CH_3 group is laterally substituted at ortho position to the carboxylate unit as under:

Smectic group efficiency order: -Br > -OCH_3 > -Cl
Nematic group efficiency order: Br > -OCH_3 > -Cl
Thus, smectic and nematic group efficiency order is same when laterally substituted methyl group is present, in azoester homologous series.

CONCLUSION

A new homologous series of azoester mesogens with –COO- and -N=N- central bridges is synthesized by treating p-n-alkoxy benzoyl chloride with p- methoxy-m'-methyl-p'-hydroxy azobenzene [3,4,7]. The order of smectic and nematic group efficiency is same i.e. -Br >- OCH_3 > -Cl . The order for early commencement of mesophase is –Br > -OCH_3= -Cl for smectic and -OCH_3 = -Br = -Cl for nematic.

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