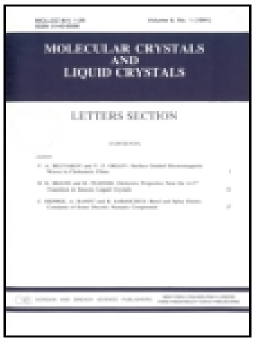

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Study of Mesomorphism Through a Novel Homologous Series and Its Relation to Molecular Structure

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A novel homologous series 4-(4′-n-alkoxy benzoyloxy)-3-chloro phenyl azo,3″,4″-dichlorobenzenes was synthesized with a view to understand and establish the relation between mesomorphism and the molecular structure. The novel series consists of 12 members, which showed commencement of monotropic nematic mesophase formation from the butoxy homologue and continued up to the hexadecyloxy homologue without exhibition of a smectic mesophase. The textures of the nematic mesophase are threaded or Schlieren in type. Transition temperatures were determined by an optical polarizing microscope equipped with a heating stage. Isotropic-nematic transition curve of the phase diagram behaved in normal manner with exhibition of odd-even effect. Solid-isotropic transition curve behaved descending tendency by adopting zigzag path up to the pentyloxy homologue; which include methoxy to propoxy homologues as nonmesomorphic derivatives. Thermal stability for the nematic is just a few degrees (1°C to 2°C). Analytical and spectral data support the molecular structures. The mesomorphic properties of present novel series are compared with structurally similar other known homologous series.

Keywords Liquid crystals; monotropy; mesomorph; mesomorphism; nematic

Introduction

Thermotropic mesomorphic substances exhibit mesomorphism peculiarities based on the variations of temperature and the range of temperature depending upon their individual molecular rigidity and flexibility [1–3] generated from respective molecular structure. Molecular structure causing suitable magnitudes of anisotropic forces of intermolecular end to end attractions [4] as a consequence of favorable molecular rigidity and flexibility can yield statistically parallel orientational order of molecules in floating condition giving rise to formation of nematic mesophase. Present investigation is planned to synthesize an azoester molecular consisting of three phenyl rings bridged through —COO— and —N=N— central groups [5] left n-alkoxy (–OR) terminal end group as well as three chloro [6–8] group substituted at middle (meta) and third phenyl ring (meta and para) as lateral and terminal positions.

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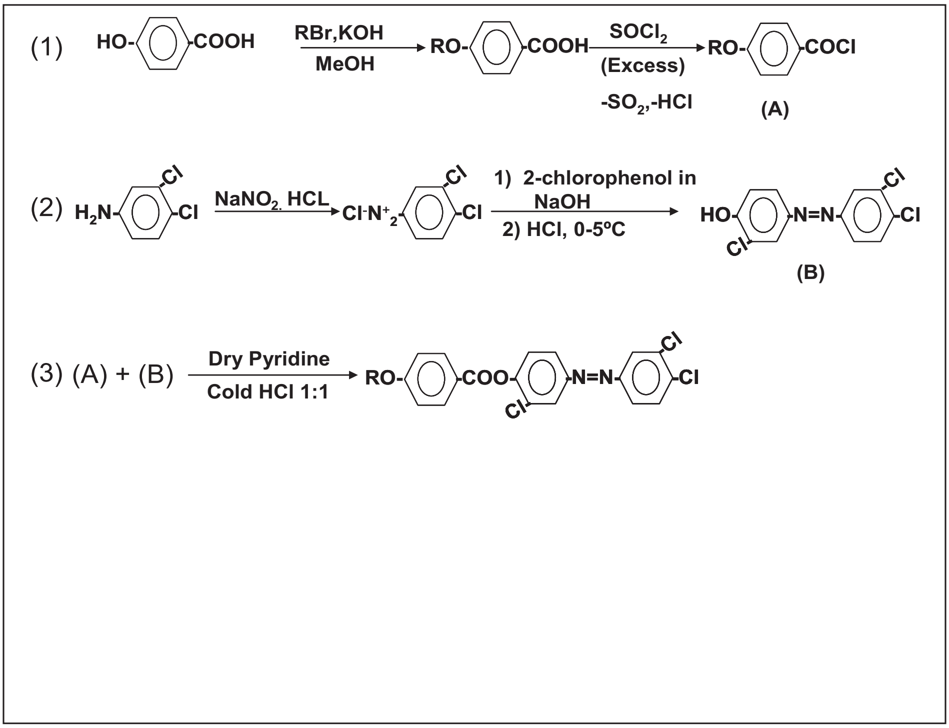
Experimental

Synthesis

4-n-Alkoxy benzoic acids were alkylated by suitable alkylating agents (R-X) by modified method of Dave and Vora [9]. An azo dye 4-hydroxy-3-chloro phenyl azo-3′-4′-dichlorobenzene was prepared by usual established method of diazotization [10, 11]. The final, azo ester homologues were prepared by condensing the various 4-n-alkoxy benzoic acids through their corresponding acid chlorides with an azo dye common component in dry cold pyridine [12]. The azo-ester novel homologues were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained. 4-Hydroxy benzoic acid, alkyl halides, MeOH, EtOH, KOH, HCl, 2-chlorophenol, 3,4-dichloro aniline, thionyl chloride, pyridine, etc. required for synthesis were used as received, except for solvents, which were purified and dried prior to sue. The synthetic route to the series is shown in Scheme 1.



Where R = C_nH_{2n+1}; n = 1,2,3,4,5,6,7,8,10,12,14,16

Scheme 1. Synthetic route to the series. Series: 4-[4′-n-Alkoxy benzoyloxy]-3-chlorophenyl azo-3′′,4′′-dichlorobenzenes.

Characterization

Representative members of the novel homologous series were characterized by elemental analysis (Table 1), infra red spectra, ^{1}HNMR spectra, mass spectra. Microanalysis for C,H,N analysis was carried out by Perkin-Elmer PE 2400 CHN analyser, IR spectra were performed

Table 1. Elemental analysis for methoxy, ethoxy, and propoxy derivatives

		Elements% found (% calculated)		
Sr. no.	Molecular formula	C	H	N
1	$C_{20}H_{13}N_2O_3Cl_3$	54.26 (55.10)	3.09 (2.98)	6.49 (6.42)
2	$C_{21}H_{15}N_2O_3Cl_3$	56.21 (56.06)	3.46 (3.33)	6.55 (6.22)
3	$C_{22}H_{17}N_2O_3Cl_3$	57.08 (56.95)	3.71 (3.66)	5.98 (6.04)

on Perkin Elmer spectrum GX and ^{1}HNMR spectra were recorded on a Bruker instrument using $CDCl_3$ as solvent. The texture of the nematic phase and transition temperatures were determined by optical polarizing microscopy equipped with a heating stage.

Analytical Data

Spectral Data

^{1}HNMR in ppm for the octyloxy derivative: 1.315 [s,$-(CH_2)_n$ of $-OC_8H_{17}$], 4,055 (t, $-O-CH_2-CH_2-$ of $-OC_8H_{17}$), 6.973 and 8.204 (dd, p.sub phenyl ring),

^{1}HNMR in ppm for the dodecyloxy derivative: 1.27 [s,$-(CH_2)_n$ of $-OC_{12}H_{25}$], 4,05 (t, $-O-CH_2-CH_2-$ of $-OC_{12}H_{25}$), 6.903 to 7.018 and 7.257 to 7.951 (m,tri.substituted phenyl ring), 8.025, 8.067, 8.308, 8.319, (dd, p. substituted phenyl ring).

IR in cm^{-1} for hexyloxy derivative: 3421.5 H-bonded $-OH$, 2929.7, 2858.3 confirms alkyl group, 1722.3, 1249.8, 1170.7 confirms $-COO-$, 1078.1 $C-O$ of ether, 1423.4 confirms $-N=N-$ group, 1043,1024 Ar-Cl linkage, 893 and 819.7 confirms 1,2,4 tri. Sub aromatic ring, 840.9 confirms p-sub benzene ring.

IR in cm^{-1} for decyloxy derivative: 3427.3 H-bonded $-OH$, 2922, 2852.5 confirms alkyl group, 1722.3, 1232.4, 1170.7 confirms $-COO-$, 1078.1 $C-O$ of ether, 1423.4 confirms $-N=N-$ group, 1045.3,1024.1 Ar-Cl linkage, 893 and 819.7 confirms 1,2,4 tri. Sub aromatic ring, 840.9 confirms p-sub benzene ring.

Mass Spectra

Mass spectra for butoxy derivative: Molecular formula $C_{23}H_{19}N_2O_3Cl_3$ Calculated Molecular weight 477.5. Practical mass observed by Mass spectroscopy 477.

Texture of Nematic Phase by Miscibility Method

Pentyloxy derivative ——————→Threaded nematic
Heptyloxy derivative ————→Schlieren nematic

Results and Discussion

Azodye, 4-hydroxy-3-chlorophenylazo-3′-4′-dichlorobenzene (M.P. 122°C) is not liquid crystalline. However, liquid crystal property is induced on linking 4-n-aloxy benzoic acids from butoxy homologue of a novel series in monotropic manner, as nematogenic phase. Azoester, novel homologues showed their transition temperatures lower than the corresponding n-alkoxy benzoic acids. Methoxy to propoxy homologues are nonmesomorphic,

Table 2. Transition temperatures of series in °C

		Transition temperature in °C		
Compound no.	n-alkyl group (—C_nH_{2n+1}) (n)	*Sm*	*Nm*	Isotropic
1	1	—	—	178.0
2	2	—	—	169.0
3	3	—	—	116.0
4	4	—	107.0	110.0
5	5	—	97.0	114.0
6	6	—	99.0	108.0
7	7	—	87.0	102.0
8	8	—	92.0	99.0
9	10	—	83.0	98.0
10	12	—	75.0	94,0
11	14	—	72.0	91.0
12	16	—	78.0	87.0
Sm: Smectic	*Nm:* Nematic			

Where R = C_nH_{2n+1}; n = 1,2,3,4,5,6,7,8,10,12,14,16.

butyloxy to hexadecyloxy homologue derivatives are mesomorphic with exhibition of nematic mesophase in monotropic manner and, without exhibition of any smectogenic character. Transition temperatures (Table 2) as determined by an optical polarizing microscopy with heating stage, plotted versus the number of carbon atoms present in n-alkyl chain of the left n-alkoxy terminal end group gives rise to a phase diagram (Figure 1); showing phase behavior through solid-isotropic and isotropic-nematic transition curves. Solid-isotropic transition curve partly adopt a zigzag path of rising and falling (up to pentyloxy homologue) and then possesses descending tendency as series is ascended without adopting zigzag path. Isotropic-nematic transition curve follows descending tendency as series is ascended with exhibition of odd-even effect. Isotropic-nematic transition curve is extrapolated [13, 14] to third member (Odd homologue) of a novel series following trend of a curve to determine and predict its latent transition temperature (LTT) for nematic (116°C). Thus, both transition curves, (viz. solid-isotropic and isotropic-nematic) behaved in normal manner. Transition curves for odd and even homologues in isotropic-nematic curve merges into each other at decyloxy homologue and then, odd–even effect disappears. Analytical, spectral data agreed with the molecular structures of the respective homologues. Thermal stability for nematic is one or two degrees (or few degree) with uncertainty of its exactness, to determine the degree of mesomorphism or phase length. However, the transition temperatures for the nematogenic mesophase persistence is exactly detectable below isotropic temperature as shown in Table 2 in bracket under column, headed by Nm. Mesomorphic behaviors of series, gradually varies from homologue to homologue as series is ascended. Thus, present homologous series is relatively low melting type with predominancy of nematogenic character in monotropic condition and absence of smectogenic character.

Linking of a phenyl ring with n-alkoxy terminal end group with a nonmesomorphic azo dye has increased molecular aromaticity, length, molecular rigidity and flexibility, molecular polarity, and polarizability resulted to induce mesomorphism in irreversible manner from and beyond fourth homologue of a novel series. Lowering of transition temperatures of the homologues, than the corresponding n-alkoxy acids and their disappearance of dimerization

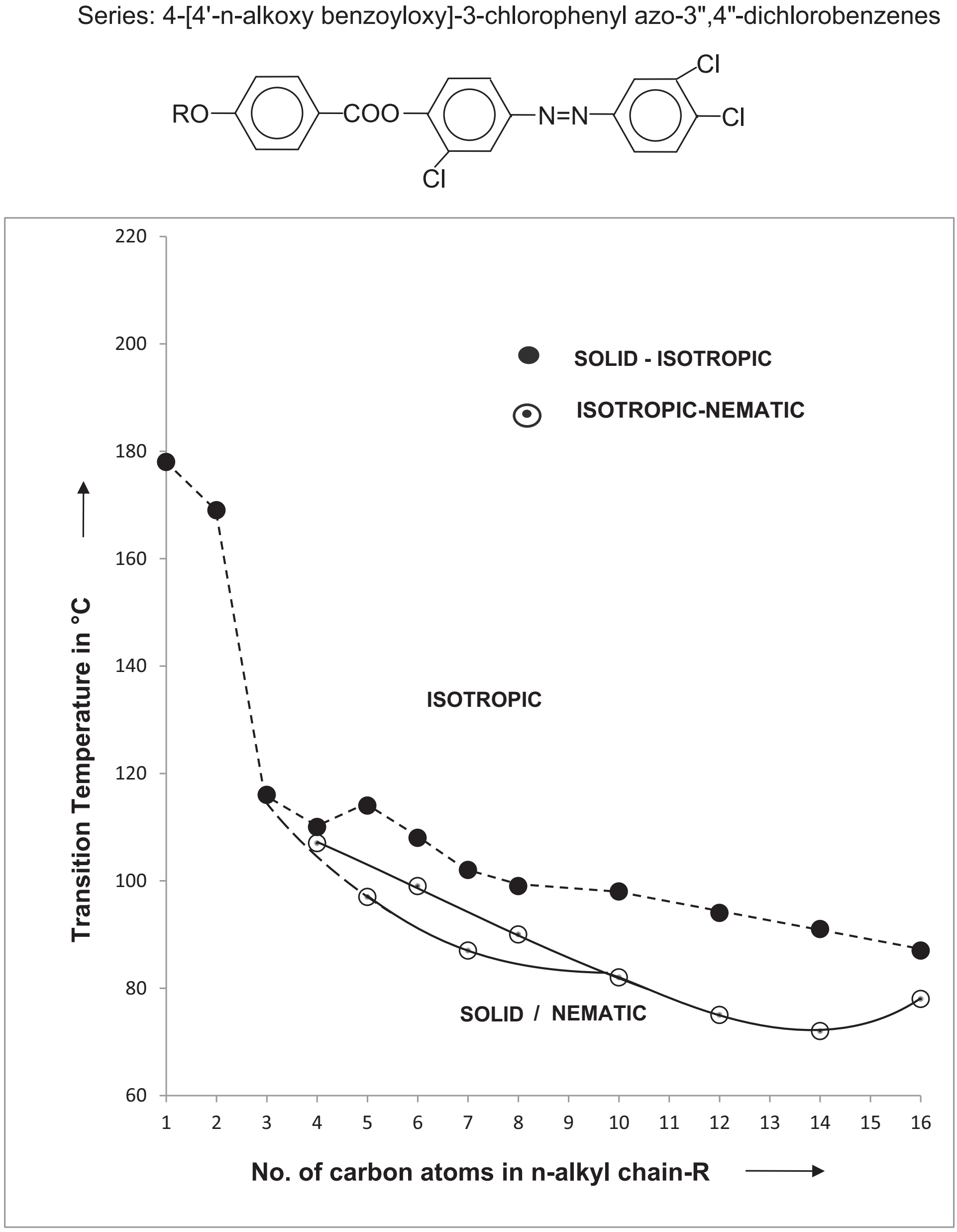


Figure 1. Phase behavior of series.

is attributed to the breaking of hydrogen bonding of n-alkoxy acids through esterification process. Twelve homologues of a thermotropic homologous series, directly transform into the isotropic liquid state, on gradual heating of a sample substance under a polarizing microscope. Thus, sample substance observed under a polarizing microscope is considered thermodynamically as an open system and the rest of the universe is then considered as the thermodynamic surroundings, that is, the exchange of heat energy takes place between a system and the surroundings. As temperature rises of a system, the supplied heat from

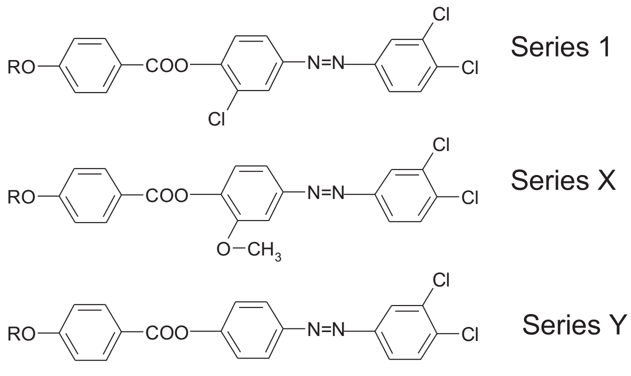


Figure 2. Structurally similar homologous series.

surroundings weakens the intermolecular end to end and other attractive forces, and finally, smooth breaking of crystal lattices sharply transform into isotropic melt at corresponding melting temperature. Then, isotropically melted mass is allowed to cool without any disturbing event, the homologues from and beyond butoxy derivative releases heat energy from a system to surroundings. As a consequence of cooling the isotropic melt, the molecules of homologue system set themselves and acquire statistically parallel orientational order in floating condition irreversibly at monotropic temperature, below isotropic temperature, under the influence of suitable magnitudes of anisotropic forces of end to end intermolecular attractions. But, the nematogenic mesophase stabilization energy is insufficient to prolong the mesophase stabilization, and immediately transforms the sample substance into solid crystalline state from mesomorphic state. Thus, entropy ($\Delta S = \Delta H/T$) of a system increase on heating a system and then decreases on cooling a sample, which observed under polarizing microscopy. Absence of smectogenic character is attributed to the high crystallizing tendency of nematogenic mesophase without passing through smectogenic mesophase, due to inadequate suitable magnitudes of anisotropic forces of intermolecular attractions which hinders lamellar packing of molecules in the crystal lattices of homologues concerned. Two opposing forces [4, 5, 6] viz (i) reducing intermolecular attractions by broadening molecules through laterally substituted two chloro groups and (ii) the enhancing intermolecular attractions by increasing molecular polarizability operating at a time causes predominancy of the force (i), that is, the reducing intermolecular anisotropic forces of intermolecular attractions, which hinders the enantiotropically nematogenic mesophase formation as well as smectogenic mesophase formation in the present series. The diminishing tendency for odd–even effect observed for isotropic-nematic transition curve, from and beyond decyloxy homologue is, due to the coiling or bending or flexing or coupling of longer n-alkyl chain of left n-alkoxy terminal end group to the major axis of the core molecule for higher homologues. Exhibition of odd–even effect, alternation of transition temperatures and variations of liquid crystal properties from homologue to homologue in the same present series are attributed to the progressive and sequential addition of methylene unit or units in left n-alkoxy terminal end group affecting suitable or unsuitable anisotropic forces of end to end intermolecular attractions. The extrapolation of isotropic-nematic transition curve to the third odd member of a series merges into solid-isotropic transition temperature indicates that, there is no possibility of the formation of nematic or smectic phase, either enantiotropically or monotropically. Relatively low melting behavior of a series and shorter mesophase length are attributed to the predominancy of the weaker intermolecular adhesion forces

(i) operated by broadening of the molecules. The mesomorphic properties of a presently investigated series 1 are compared with other known structurally similar homologous series X [15] and Y [16] as shown in Fig. 2.

Homologous series-1 and series X, Y chosen for comparing mesomorphic properties as shown in Fig. 2 are structurally identical with respect to three phenyl rings bonded through $-COO-$ and $-N{=}N-$ central bridges, left and right terminally situated end groups –OR and $-Cl$, another $-Cl$ group substituted at meta position to $-N{=}N-$ group on third phenyl ring as lateral group. However, series 1,X and Y differ only with respect to a group $-Cl$, $-OCH_3$ and $-H$ substituted at ortho position to $-COO-$ meta position to $-N{=}N-$ on middle phenyl ring respectively. Therefore, variations in mesomorphic properties and their degree of mesomorphism vary, due to the varying laterally substituted $-Cl$, $-OCH_3$, and $-H$ group at the middle phenyl ring at the identical position from $-N{=}N-$ central bridge. Thus, variations can be co-related with differing molecular polarity, polarizability, molecular rigidity and flexibility, etc. related to combine effect of anisotropic forces of intermolecular lateral and terminal attractions. Following Table 3 represents thermal stabilities, commencement of mesophases, type of mesophase etc for series 1, X and Y.

Homologous series 1 and X are monotropically either nematic or smectic respectively. However, series Y is predominantly nematic and partly smectic. Series 1 and X structurally differ by only lateral substitution at identical position on middle phenyl ring by $-Cl$ and $-OCH_3$ group. The $-OCH_3$ group relatively being more polar [4, 6] than $-Cl$, can contribute more, toward molecular polarity and polarizability. Thus, overall molecular rigidity, flexibility, polarity, and polarizability including other intermolecular adhering, anisotropic forces facilitated, lamellar packing of molecules in crystal lattices to form interlayered linking in floating condition for series-X below isotropic temperature; while chloro group under the same condition in series 1 generate, such a little bit less magnitudes of anisotropic forces by combine effect of lateral and terminal end to end attractions, that, molecules of series 1 set an angle less than 90 degree to arrange themselves, statistically parallel orientational order below isotropic temperature under floated movement, without formation of lamellar packing of molecules in their crystal lattices. Thus, homologous series 1 exhibit only nematic phase while, series X, exhibit only smectic phase in irreversible or monotropic manner. Now on comparing series Y with series 1, the –chloro group bonded at middle phenyl ring is eliminated or to say replaced by H, the mesomorphic behavior of series Y is drastically uplifted. Only elimination of $-Cl$ group from middle

Table 3. Average thermal stability in °C

Series→	Series 1	Series X	Series Y
Smectic-isotropic or smectic-nematic or nematic-smectic or isotropic-smectic commencement of smectic phase	—	1 or 2 degree or few degree (C_5-C_{16}) C_5	106.6 (C_6-C_{16}) C_6
Nematic-isotropic or isotropic-nematic commencement of nematic phase	1 or 2 degree or few degree (C_4-C_{16}) C_4	—	156.25 (C_1-C_{16}) C_1

phenyl ring modifies molecule of series Y as long linear path like without any steric hindrances keeping molecular polarizability as equal as of series 1. Thus, intermolecular closeness strengthened to raise suitable magnitudes of anisotropic forces of intermolecular attraction drastically high enough to resist, externally exposed thermal vibrations which permitted the molecules of series Y to build their lamellar packing and interlinked layers in their crystal lattices as well as subsequently it allowed to maintain statistically parallel orientational molecular order due to adequate end to end attractions. Thus, smectic and nematic mesophase exhibited for definite range of temperature persisted enantiotropically in case of series Y. Thus, even a smallest structural change can yield the drastic change in the mesomorphic behavior of a substance. Now as regard to the comparison of commencement of mesophase formation, the nematic mesophase commences from butyloxy homologue of a series-1, from very first member of a series Y and it does not commence till the last homologue of a series X. Thus, type of nematogenic behavior is attributed to the suitable or unsuitable magnitudes of end to end intermolecular anisotropic forces of attractions occurred as a consequence of varying molecular rigidity and/or flexibility which varies by only laterally substituted groups $-Cl$, $-OCH_3$, and $-H$, keeping both terminal end groups ($-OR$ and $-Cl$) unchanged. Thus, intermolecular lateral attractions plays the major role to the commencement of nematic phase. The smectic mesophase commences from hexyloxy homologue for series Y, pentyloxy homologue for series X and it does not commence till the last homologue for the novel series 1 under present investigation. The early or late commencement of smectic phase depend upon early or late commencement of lamellar packing of molecules in their crystal lattices, which in turn depends upon the extent of noncoplanarity of the respective molecules of different molecular structures. Thus, extent of noncoplanarity played by differing individual group polarities of $-Cl$, $-OCH_3$ and $-H$ substituted at middle phenyl ring at identical position. Thus, differing degree of molecular coplanarity results, commencement of smectic phase from respective order of coplanarity. The variations in mesomorphic properties from series to series for the same homologue arise from uncommon molecular part or the differing entity of the corresponding molecular structure. Differing entity may be terminal end group, lateral group, position of same group or groups on same or different phenyl ring or rings, central group or groups, etc.

Conclusions

- The group efficiency order derived on the basis of thermal stability and early commencement of mesophases with reference uncommon to lateral substitution is as under.
- Thermal stabilities

$$\text{Smectic}: \quad -H > -OCH_3 > -Cl$$

$$\text{Nematic}: \quad -H > -Cl > -OCH_3$$

- Commencement of mesophase

$$\text{Smectic}: \quad -OCH_3 > -H > -Cl$$

$$\text{Nematic}: \quad -H > -Cl > -OCH_3$$

- Present investigated novel series is predominantly monotropically nematogenic without exhibition of smectogenic character and low melting type.
- Elimination or substitution of a same functional group at same position can create a drastic change in liquid crystal behavior.
- Mesophase behavior is very sensitive and susceptible to molecular structure.
- Molecular rigidity and flexibility of favorable magnitudes can cause suitable magnitudes of anisotropic forces of intermolecular attractions which can induce liquid crystalline property in a substance.
- Variations in liquid crystal property and the degree of liquid crystallinity between two different homologous series depend upon uncommon part of a molecular structure.

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