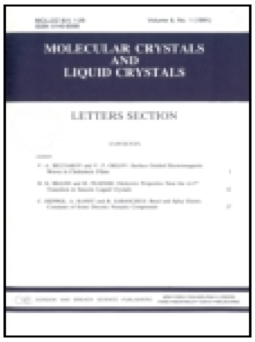

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Mesomorphism Dependence on Molecular Flexibility in an Azoester Series

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A novel azoester homologous series with a flouro terminal end group was synthesized and evaluated for mesomorphic properties. The novel homologous series consists of 12 members. The first two-third members of the series are nonmesogenic. The butyloxy to decyloxy homologues are enantiotropic nematogenic and the rest of the mesogenic homologoues are enantiotropic smectogenic only. Transition temperatures and textures of the mesophases were observed through an optical polarizing microscope equipped with a heating stage. The textures of the nematic phase are threaded or Schlieren as judged by a miscibility method and those of the smectic phase are of the type A or C. A phase diagram is used to illustrate the mesomorphic behavior across the series. Analytical and spectral data confirm the molecular structures of the homologues. Thermal stabilities of smectic and nematic mesophases are 114.3°C and 137.0°C respectively. The mesogenic phase lengths for smectic and nematic are vary from 8°C to 26°C and 26°C to 43°C respectively.

Keywords Liquid crystals; mesomorphism; nematic; smectic

Introduction

Liquid crystal material are useful in technological applications, such as display devices, optical imaging, light emitting diodes, anisotropic network, semiconductor materials, etc. [1]. Biomaterials in combination with thermotropic liquid crystals improves the performance of liquid crystal displays using LC physical gel consisting of acid-base gelators [2]. Benzoyloxy and cinnamoyloxy derivatives are useful in agricultural and pharmaceutical fields. Chalcones derivatives are useful as anti-inflammatory anticancer and antioxidant [3, 4]. Thus, conventional and unconventional [5, 6] liquid crystal materials of different moieties containing ether, ester, azoeter, ethylene, etc. derivatives have been reported earlier [7–9]. The present investigation is planned to synthesize novel liquid crystal materials consisting of benzoyloxy naphthyl derivatives with n-alkoxy and fluorine as terminal end groups and —COO— and —N=N— central linking groups to understand and establish the effects of molecular flexibility[10–13] of the molecules on liquid crystal behaviors. The present investigation will include synthesis of novel compounds, their characterization by

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polarizing microscopy, mass spectrometry, IR, ^{1}HNMR spectra, elemental analysis, their comparative study of mesogenic behaviors with known series based on effects of molecular structure on liquid crystal behaviors [14, 15].

Experimental

Synthesis

4-Hydroxybenzoic acid was alkylated by suitable alkylating agents to give the required 4-n-alkoxy benzoic acids, which on further treatment with thionyl chloride gave the corresponding acid chlorides [A] by the modified method of Dave and Vora [16] and these were used directly for further reaction without purification. Azo dye p- fluoro-p'-hydroxy azonaphthalene [B] M.P. 80°C was prepared by the usual established method of diazotization [17, 18]. Components [A], i.e., 4-n-alkoxy benzoyl chloride and component [B], i.e., azo dye were condensed in dry cold pyridine to prepare the final azoester molecules by the usual etherification method [19]. Final products were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained. Transition temperatures of homologues were determined on an optical polarizing microscope equipped with a heating stage. The chemicals viz. 4-hydroxy benzoic acids, alkyl halides (R–X), methanol, ethanol, KOH, thionyl chloride, α- naphthol, p-fluoro aniline, pyridine, NaOH, etc. required for synthesis were used as received excepted solvents, which were dried and purified prior to use. The synthetic route to the novel azoester series is shown in scheme 1.

Characterization

Some of members of the novel series as the representative members were characterized by elemental analysis (Table 1), infrared spectroscopy, ^{1}H NMR spectra, mass spectrometry, and textural identification. Microanalysis was performed on EuroEA Elemental Analyzer. IR spectra were recorded on Shimadzu FTIR-8400 spectrometer, ^{1}HNMR spectra were recorded on Bruker spectrometer using DMSO-d$_6$ as a solvent and mass spectra were recorded on Shimadzu GC-MS Model No.QP-2010 spectrometer. The liquid crystal behavior and the type of textures were determined by a miscibility method on microscopic observations.

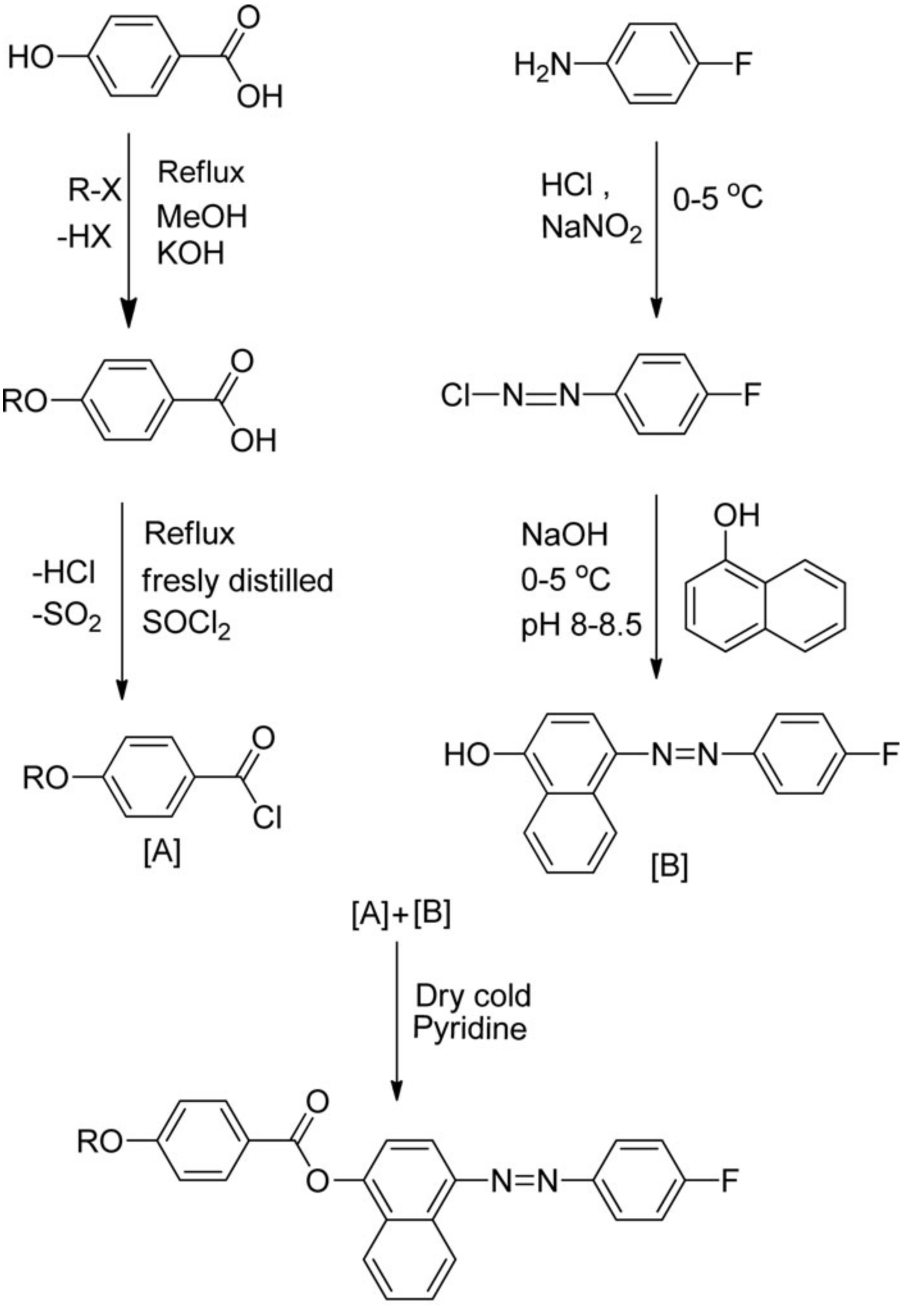
Analytical Data

Elemental Analysis (Table 1)

Spectral Data

^{1}HNMR in ppm for Hexyloxy Derivative

0.87–091 (t, 3H, $-\mathrm{CH_3}$ of $-\mathrm{OC_6H_{13}}$ group), 1.28–1.33 (4H, $\mathrm{CH_3}-\underline{\mathrm{CH_2}-\mathrm{CH_2}}-$), 1.74–1.77 (2H, $-\underline{\mathrm{CH_2}-}\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}-$), 4.06–4.08 (t, 2H, $-\mathrm{CH_2}-\mathrm{O}-$), 6.85–8.71 (12H, Aromatic Hydrogen), 8.21–8.74 (d, 1H, in phenyl ring ortho to $-\mathrm{N}=\mathrm{N}$-group),The NMR data are reliable with the molecular structure.



4(4'-n-Alkoxy benzoyloxy) naphthyl azo-4'' fluoro benzenes

Where, R= C_nH_{2n+1} and n= 1 to 8,10,12,14 and 16.

Scheme 1. Synthetic route to the novel series.

Table 1. Elemental analysis for (1) Ethyloxy (2) Butyloxy (3) Tetradecyloxy derivatives

		Elements % Found			Elements % calculated		
Sr. no.	Molecular formula	C	H	N	C	H	N
1	$C_{25}H_{19}FN_2O_3$	72.49	4.60	6.73	72.45	4.62	6.76
2	$C_{27}H_{23}FN_2O_3$	73.24	5.27	6.35	73.29	5.24	6.33
3	$C_{37}H_{43}FN_2O_3$	76.23	7.42	4.86	76.26	7.44	4.81

^{1}HNMR in ppm for Dodecyloxy Derivative

0.83–0.89 (t, 3H, $-CH_3$ of $-OC_{12}H_{25}$ group), 1.26–1.30 (m, 16H, $CH_3-\underline{CH_2-(-CH_2-)_6 -CH_2-}$), 1.43 ($-O-$ $CH_2-CH_2-\underline{CH_2-}$), 1.74–1.77 (m, 2H, $-\underline{CH_2}-CH_2-O-$), 4.07 (t, 2H, $-\underline{CH_2}-O-$), 6.84–8.12 (12H, Aromatic Hydrogen), 8.22–8.72 (d, 1H, in phenyl ring ortho to $-N=N-$group),The NMR data are reliable with the molecular structure.

IR in cm^{-1} for Butyloxy Derivative

2852, 2920 (C—H Str. of $(-CH_2-)_n$ group of $-OC_7H_{15}$), 1440, 1604 (aromatic C=C Str.), 3068, (C—H Str. of aromatic ring), 1010, 1068, 1168, 1267 (C—O Str. of —COO-group), 1728 (C=O, Str. of —COO— group), 1139 (C—O—C—), 750, 848, 698 (pera, ortho, and meta substituted phenyl ring) 1604 (—N=N— Str.). The IR data are consistent with the molecular structure.

IR in cm^{-1} for Octyloxy Derivative

2852, 2933 (C—H Str. of $(-CH_2-)_n$ group of $-OC_{12}H_{25}$), 1465, 1506, 1579 (aromatic C=C Str.), 3070 (C—H Str. of aromatic ring), 1066, 1170 (C—O Str. of —COO-group), 1732 (C=O, Str. of —COO-group), 1143 (C—O—C—), 750, 842, 692 (pera, ortho, and meta substituted phenyl ring).1604 (—N=N— Str.). The IR data are consistent with the molecular structure.

Mass Spectra of Heptyloxy Derivative

m/z (rel. int%): 485 $(M)^+$, 249, 235, 115, 99

Mass Spectra of Decyloxy Derivative

m/z (rel. int%): 527$(M)^+$, 385, 277, 249, 141

Results and Discussion

The novel homologous series 4-[4′-n-alkoxy benzoyloxy]nephthylazo 4′-fluoro benzenes generates mesomorphism from the butyloxy homologue to the hexadecyloxy homologue, but the shorter chain homologues are not liquid crystalline. The butyloxy to decyloxy homologues are enantiotropic nematogenic, the dodecyloxy, tetradecyloxy, and hexadecyloxy homologues are enantiotropic smecogenic. The transition temperatures of the series, as determined by optical polarizing microscopy equipped with a hot stage (Table 2), are

Table 2. Transition temperatures in °C

Compound no.	n-alkyl chain C_nH_{2n+1} (n)	Sm	N	Isotropic
1	1	—	—	160.0
2	2	—	—	175.0
3	3	—	—	145.0
4	4	—	130.0	156.0
5	5	—	122.0	143.0
6	6	—	109.0	140.0
7	7	—	99.0	131.0
8	8	—	83.0	124.0
9	10	—	85.0	128.0
10	12	92.0	—	118.0
11	14	94.0	—	115.0
12	16	102.0	—	110.0

Sm = Smectic, N = Nematic.

plotted against the number of carbon atoms in the terminal chain. The like or related points are linked to give smectic–isotropic, nematic-isotropic and solid-isotropic/mesomorphic curves to represent a phase diagram (Fig. 1) showing the phase behaviors of the novel series. The solid-isotropic/mesomorphic transition curve follows a zigzag path of rising and falling values up to the third member of the series, then it alternatively descends continuously to the octyloxy homologue and then it ascends to the hexadecyloxy homologue with overall descending tendency as series is ascended. A smectic-isotropic transition curve

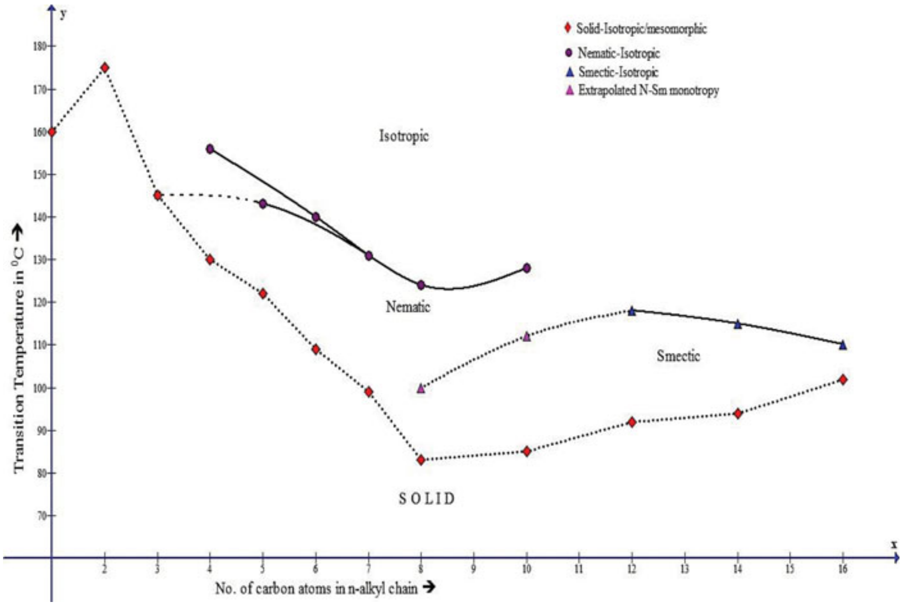


Figure 1. Phase behavior of series.

is descended from the dodecyloxy to hexadecyloxy homologues without the exhibition of an odd–even effect. The smectic-isotropic transition curve is extrapolated [20, 21] from the even members, decyloxy, and octyloxy, which are actually smectogenic in character, and the extrapolated transition curve suggests a monotropic N-Sm transition temperatures of 113°C and 99°C. Re-examination of the decyloxy and octyloxy samples on polarizing microscopy still did not show monotropic nematic behavior. The nematic-isotropic transition curve shows a descending trend from the butyloxy to decyloxy derivatives with exhibition of an odd–even effect and alternation of transition temperatures. Thereafter the nematogenic mesophase ceased to appear for the higher homologues. The nematic-isotropic transition curves for odd homologues (7 and 5) were extrapolated [22, 23] up to the third member of the series to magnify odd–even effect. All three transition curves of the phase diagram show phase behavior in a normal manner.

The odd–even effect disappears from and beyond the heptyloxy homologue for the longer n-alkoxy chain. The mesomorphic behavior varies from homologue to homologue in the present series. The present novel series is predominantly nematogenic and partly smectogenic with middle ordered melting type, whose mesomorphic phase lengths vary between 08°C to 43°C at the hexadecyloxy and decyloxy homologues respectively.

The dimerization of n-alkoxy benzoic acids disappeared by esterification process due to breaking of hydrogen bonding between two molecules of 4-n-alkoxy benzoic acids, azodye 4-hydroxy naphthylazo 4′-fluoro benzene is a nonmesogenic component of a novel azoester molecule. However, linking the azo section with the 4-n-alkoxy benzoic acid through corresponding acid chloride increases molecular length and breadth which causes an increase in molecular polarity and polarizibility to withstand against the external force operating by thermal vibrations. The laterally substituted phenyl ring of naphthalene unit increases molecular rigidity which increases resistivity against exposed thermal vibrations, through molecular polarity and polarizibility. However, induced polarity and polarizability causing end to end and lateral attractions are of unsuitable magnitudes for methyloxy to propyloxy homologues to resist exposed thermal vibrations. Therefore, they sharply transform into isotropic liquid without passing through an intermediate state of existence between crystalline solid and isotropic liquid; as a consequence of unfavorable magnitudes of molecular rigidity and flexibility. But molecular rigidity and flexibility of the molecules from and beyond butyloxy homologue of a present novel series become favorable to induce mesogenic mesophase within definite range of temperature. The resultant molecular rigidity and flexibility generates suitable magnitudes of anisotropic forces of end to end and lateral intermolecular attractions of appropriate intermolecular closeness for mesomorphic homologues, which causes the disalignment of molecules at an angle less than 90 degree with the plane of a floating surface. The molecules of butyloxy homologue to decyloxy homologue under the influence of end to end attractions floats with statistically parallel orientational two dimensional orders within some degree temperature range, giving rise to appearance of nematogenic mesophase. The molecules of dodecyloxy, tetradecyloxy, and hexadecyloxy homologues with relatively more favorable magnitudes of intermolecular attractions bear lamellar packing of molecules in their crystal lattices which form focal conic molecular networking which float on the plane of a surface as sliding layers within definite temperature range with appearance of smectic mesophase formation. The variation in mesomorphic properties from homologue to homologue in the present series is attributed to the sequential addition of methylene unit or units. The disappearance of odd-even effect from and beyond heptyloxy homologue for relatively longer n-alkyl chain is attributed to the coiling or bending or flexing or coupling of n-alkyl chain with major axis of the core structure. Thus, uncertainty in the status of n-alkyl chain of higher homologues

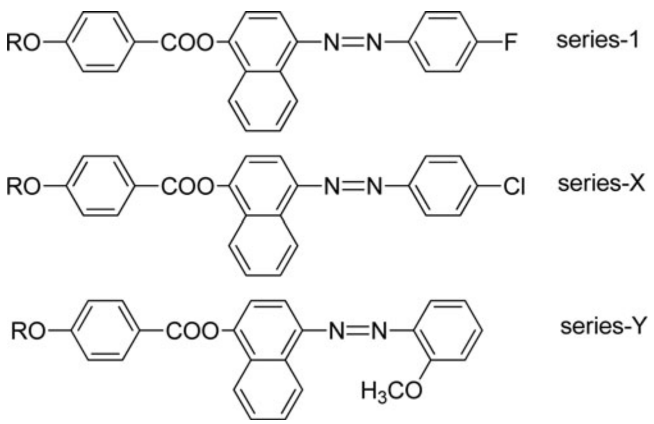


Figure 2. Structurally similar series.

plays the role for presence or absence of prolongation of odd–even effect through n-alkyl chain of n-alkoxy terminal end group. The mesomorphic behavior of presently investigated homologous series-1 is compared with a structurally similar other known homologous series X [23] and Y [24]; as shown in following Fig. 2.

Homologous series 1 and series X and Y chosen for comparison are identical with respect to two phenyl rings bonding two fused phenyl rings (naphthyl) through —COO— and —N=N— central bridges which builds up molecular rigidity. i.e., the effects due to molecular rigidity for all the three series 1, X, and Y play an equivalent role in inducing mesomorphism. But, they differ with respect to their molecular flexibility which immerges from changing n-alkyl chain length from homologue to homologue in the same series and changing terminal end group —F, —Cl and lateral —OCH_3 group for the same homologue from series to series. Thus, flexibility contribution to the mesomorphism varies from homologue to homologue in the same series and for the same homologue from series to series. Therefore, the mesomorphic behavior and the degree of mesomorphism depend upon the differing features of each series under comparison and discussion. Following table 3 represents some mesomorphic behavior like, thermal stabilities for smectic and nematic mesophase, commencement of mesophases, mesomorphism exhibition by homologues, etc.

Table 3 indicates the following.

- Homologous series-1 exhibited smectogenic and nematogenic mesomorphism; whereas series X and Y selected for comparison exhibited only nematogenic mesomorphism.

Table 3. Average thermal stabilities in °C

Series →	1	X	Y
Smectic-isotropic	114.3	—	—
Commencement of smectic mesophase	(C_{12}–C_{16}) C_{12}	—	—
Nematic-isotropic	137.0	129.9	149.2
Commencement of nematic phase	(C_4–C_{10}) C_4	(C_3–C_{16}) C_3	(C_6–C_{14}) C_6

- Nematogenic mesomorphism commences from C_4, $C_{3,}$ and late from C_6 carbon atom for series 1, X, and Y respectively.
- Smectogenic property commences from C_{12} carbon in case of series 1 but it does not commence till the last member of the series X and Y.
- Mesomorphic phase length vary from 08°C to 43°C for series 1, while it ranges from 31°C to 50°C for series X and 28°C to 65°C for series Y.
- Smectic thermal stability of series 1 is 114.3°C while smectic mesophase formation did not stabilize and facilitate for series X and Y.
- Nematic mesophase formation facilitated and stabilized for certain degree of mesomorphism.

The electron attracting and electron accepting tendency of terminally/laterally situated fluorine, chlorine, and oxygen atom are in the order of $F > O > Cl$. Therefore, the bond polarity of a bond linking carbon atom of a third phenyl ring and terminal end group (i.e., $-\mathrm{C}^{+\delta}-\mathrm{F}^{-\delta} < -\mathrm{C}^{+\delta}-\mathrm{O}^{-\delta}_{-} < -\mathrm{C}^{+\delta}-\mathrm{Cl}^{-\delta}$) decreases from F to Cl. Therefore, end to end intermolecular attractions and the degree of molecular flexibility from homologue to homologue in the same series and for the same homologue from series to series as well as extent of molecular co-planarity undergo variations accordingly. However, the lateral substitution of $-OCH_3$ group and the varying atomic size of $-F$ and $-Cl$ contribute to the molecular polarizability toward suitable magnitudes of intermolecular attractions, intermolecular closeness positively, excluding the negative effect to intermolecular attractions by steric hindrance due to ortho substituted $-OCH_3$ to $-N{=}N-$ central bridge, etc. Thus, the next effects of the suitable magnitudes operating intermolecular attractions by changing molecular flexibility, inducing anisotropic forces to cause mesophase formation either smectic or/and nematic. The net intermolecular anisotropic forces of intermolecular attractions are sufficient to cause lamellar packing of molecular in the crystal lattices of dodecyloxy, tetradecyloxy, and hexadecyloxy homologues of series 1 which, forms sliding layers to show only smectic mesophase formation and then the rest of the mesomorphic homologues of series 1 due to absence of lamellar packing, floated with only statistically parallel orientational ordered and exhibited only nematic mesophase formation. However, under the same condition, the net anisotropic forces operating amongst the molecules of series X and Y chosen for comparison is insufficient to facilitate lamellar packing of molecules in their crystal lattices but sufficient to float with only statistically parallel orientational order from C_3 and C_6 homologues with relatively higher degree of nematogenic mesomorphism only. The highest value of nematic thermal stability is attributed to the highest polarizibility contributed by laterally substituted $-OCH_3$ polar group, which exceeded the magnitudes of end to end attractions. Absence of lamellar packing in the crystal lattices as well as unsuitable extent of noncoplanarity caused by the molecules of series X and Y, fails to facilitate interlinking of molecules to form focal conic three dimensional arrangement of layered structure. Hence, smectogenic mesophase formation is missing for the series X and Y. Thus, smectogenic mesophase commences though late from twelfth member of a series 1 but it does not commence till the last member of a series X and Y. Early statement that "naphthalene derivatives of LC are generally nematogenic" is partly supported by present investigation, but it is not universally true. Thus, variations in mesomorphic behaviors from homologue to homologue in the same series and for the same homologue from series to series depend upon changing n-alkyl chain by methylene unit or units for same series but it vary with changing right handed terminal or lateral end group for the same homologue from series to series respectively.

Conclusions

- Presently investigated naphthylazoester series is predominantly nematogenic and partly smectogenic with middle ordered melting type whose degree of mesomorphism between 8°C to 43°C.
- Fluorine is corrosive to the health; therefore, it should be carefully handled while using it.
- The group efficiency order derived for smectic and nematic mesophase formation on the basis of

  (a). Thermal stability and
  (b). The early commencement of mesophase is as under.

  a). Smectic: –F > –Cl = –OCH_3(lateral)
  Nematic: lateral –OCH_3 > –F > –Cl
  b). Smectic: –F > –Cl = –OCH_3 (lateral)
  Nematic: –Cl > –F > –OCH_3 (lateral)

- Molecular flexibility difference can cause variations in mesomorphic behaviors of a substance.
- Mesomorphic properties of a substance are sensitive and susceptible to molecular flexibility.

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