

Synthesis and characterization of λ -shaped azo liquid crystals: The effect of terminal alkoxy group

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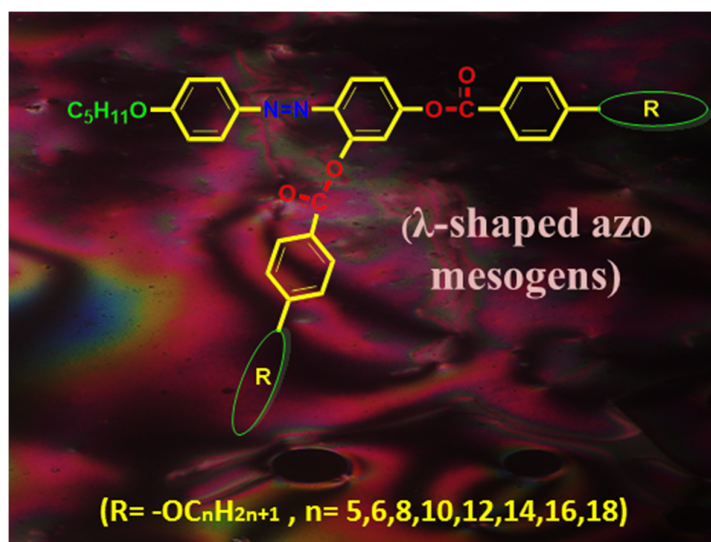
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ABSTRACT

The construction of a λ -shaped three side substituted alkoxy based molecular system (E_1-E_8) with azo-ester group was carried out and studied for liquid crystalline applications. The mesogenic behaviour and thermal stability of synthesized derivatives were checked and analyzed by POM, DSC and TGA analysis. These azo-ester based compounds show smectic C and nematic type mesomorphic properties. The observed texture patterns of the synthesized compounds are fan, broken fan, schlieren and threaded types. All derivatives shows broad temperature range of mesophase and further stabilized upto the room temperature. The structure-property relationship has been further studied to understand the effect of variable side-chain on liquid crystalline properties.

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Graphical Abstract

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1. Introduction

Liquid crystals (LCs) are a unique physical state of matter that is neither pure crystalline solid nor isotropic liquid, but the mobility of these materials is high as compared to both¹⁻³. These materials are getting much more demand in the production of electronic display devices, light-emitting materials, and other electronic applications⁴⁻⁶. Till the date, numbers of various shaped liquid crystalline compounds were reported with different properties, mesophase behavior, thermal stability and applications.

The presence of azo (-N=N-) group in the molecular systems supplies photosensitivity and tuning photo induced applications⁷. However, sometimes the presence of azo linker creates partial distraction to induce liquid crystalline properties may be due to the characteristic of a conformer. Azo linker incorporated in their side arms and supported by other linking groups, most commonly supported by ester linking units shows liquid crystalline properties⁸⁻¹⁰. Aromatic esters are recognized for LC property due to their thermal stability, ease synthesis, and relative resistance to hydrolysis, as well as the ester group conjugation connections between the two phenyl rings further linked with other linking units like Schiff-base, azo, amide etc.¹¹. Further, the different substituent group on the lateral and terminal side alters the polarizability of the aromatic ring and creates an impact on liquid crystalline properties. As a result, the literature clearly indicates that the stronger the lateral adhesion of linear molecules, the greater the stability of a mesophase, which would be reinforced by an increase in the polarity and/or polarizability of the mesogenic region of the molecule¹²⁻¹⁶.

In literature, various shaped liquid crystalline series based on azo linking group were reported¹⁷⁻²². Thaker et al.²³ reported homologous series based on azo-ester and Schiff base-azo linking group. Magdi et al.²⁴ synthesized six homologous series based on azo-ester group. Continuing to this, C. Kannan et al. prepared two homologous calamitic-shaped series based on Schiff bases with azo and ester linkage group and investigated the liquid crystalline properties²⁵. Karim and his colleagues developed azo-ester linked mesogens and also studied the effect of various terminal groups (-F, -Cl, -Br, -OCH₃, -OC₂H₅, and -OC₃H₇) on mesomorphic properties²⁶. Further, various researchers reported numbers of homologous series based on three phenyl rings and two linking groups²⁷⁻³³. Recently, Al-Hamdani et al. reported azo-phenylbenzothiazole moiety-based liquid crystals with a variety of substituents/groups at position-3 of the core benzene ring (-H, -OH, -CH₃, -Cl, -F)³⁴. Ahmed et al. synthesized twenty-four homologous compounds with 4-alkoxyphenyl azo-methine phenyl 4-(4''-alkoxyphenylazo) benzoates molecular systems and examined their mesomorphic behavior once the azo group was replaced³⁵. Furthermore, our group reported biphenyl ring based homologous series contain azo-ester linking group³⁶. Recently, Farooq et al. published a review article on liquid crystalline compounds based on azo group linked with natural products like menthol, kojic acid, cholesterol, and chalcone group³⁷. Very recently, Saad et al. reported four phenyl ring based homologous series and studied the steric effect of di-lateral methyl substituent on the mesophase behavior azo/ester/azo compounds³⁸. Yam et al. reported first tetra-fluorinated azobenzene linked imidazolium based ionic conjugates as potential thermotropic liquid crystalline drugs³⁹.

In the present study, we have designed and synthesized azo-ester based non-linear shaped material for nematogenic mesogens having terminal alkyl spacers and investigated their liquid crystalline properties and further studies the structure property relationship to understand the effect of variable alkoxy side chain on liquid crystalline properties. The proposed investigation consists of eight azo-ester based mesogens with four rings and fixed n-pentyloxy at one terminal end and variable alkoxy group on the other tail group. These nematic types of photoactive liquid crystalline materials may be further applicable for the fabrication of potential display devices such as temperature sensors, display monitors and LCDs.

2. Experimental

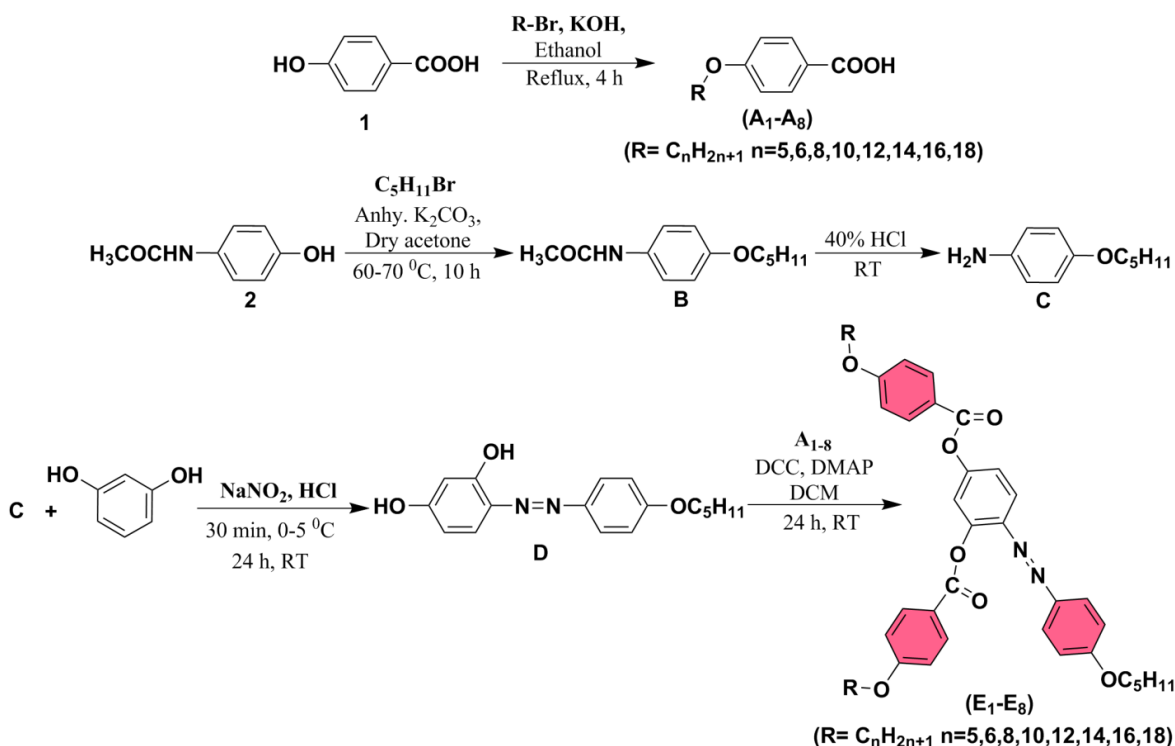
2.1. Materials

4-hydroxy benzoic acid, potassium carbonate (K₂CO₃), sodium nitrite (NaNO₂), resorcinol, and 4-hydroxy acetanilide were purchased from Avra Chemicals, India. Alkyl bromides (R-Br) were purchased from S.R.L Chemicals, India. Further, the dimethyl amino pyridine (DMAP) and *N,N'*-Dicyclohexyl carbodiimide (DCC) were purchased from Finar Chemicals, India. The solvents were dried and purified by a standard method prior to use.

2.2. Measurements

Melting points were taken on the Opti-Melt (automated melting point system). The FT-IR spectra were recorded as KBr pellets on Shimadzu in the range of 3800–600 cm⁻¹. The texture images were studied on a trinocular polarizing optical microscope (POM) equipped with a heating plate and a digital camera. ¹H NMR was recorded on a 400MHz Bruker Advance in the range of 0.5–16 ppm using CDCl₃ solvent. The phase transition temperatures were measured using the Shimadzu DSC-50 on heating and cooling rates of 10 °C/min. The thermodynamic quantities enthalpy (ΔH) and entropy (ΔS=ΔH/T) are qualitatively discussed.

2.3 Reaction scheme

Scheme 1. Synthesis of target compounds (E₁-E₈).2.4. Synthesis of compounds in present series (E₁-E₈)2.4.1. 4-n-Alkoxy benzoic acid (A₁-A₈)

4-n-alkoxy benzoic acid is prepared by using the previously established method⁴⁰.

2.4.2. Preparation of N-(4-(pentyloxy) phenyl) acetamide (B)

4-Hydroxy acetanilide (0.033 moles), n-pentyl bromide (0.033 moles), K₂CO₃ (0.087 moles) were mixed with acetone (30 ml) and stirred at 60-70 °C for 10 hours. The white color crude product N-(4-(pentyloxy) phenyl) acetamide obtained with 75% yield. The recrystallization of the crude is carried out in methanol⁴⁰.

2.4.3. Preparation of 4-(pentyloxy) aniline (C)

Hydrolysis of 4-(pentyloxy) acetamide was carried out in acidic medium. In 4-(pentyloxy) acetamide (0.5 moles) (B), 40% HCl solution (10 ml) was drop-wise added with constant stirring. The brown color product is obtained with 90% yield and further purified by liquid-liquid extraction using diethyl ether⁴⁰.

2.4.4. Preparation of (E)-4-((4-(pentyloxy) phenyl) diazenyl) benzene-1,3-diol (D)

Compound C (0.5 moles), resorcinol (0.3 moles), sodium nitrite (1.5 moles) and dilute HCl (10 ml) were mixed at 0-5 °C for 30 min. then allowed for overnight stirring at room temperature. After the completion of reaction red colored product obtained with 80% yield and recrystallized using methanol⁴⁰.

2.4.5. Synthesis of targeted compounds (E₁-E₈)

Finally targeted compounds have been prepared by esterification of compound D (1 mmol) with Compound A₁₋₈ (1 mmol) in presence of DCC (2.2 mmol) and DMAP using DCM (30 ml) solvent. Yellow to orange color product obtained with 85% yield and purified through column chromatography using eluent ethyl acetate: Hexane (20:80)⁴¹. The synthetic route of the present synthesized series is shown in Scheme 1.

2.5. Selected data of synthesized compounds (E₁-E₂)

IR Spectra of Pentyloxy in cm⁻¹ (E₁): 861 Poly methylene group of (-CH₂)_n in -OC₅H₁₁, 850 (-C-H def. tri-substituted phenyl ring -OC₅H₁₁), 961 (-C-H def. hydrocarbon in -OC₅H₁₁), 1205 (-C-O-) Str, 1291, 1410 (-C-O- str in -(CH₂)_n long

alkyl chain), 1570 (-C-H def. in -CH₂ unit in long alkyl chain), 1490 (-N=N-) azo group, 1660 (carbonyl -C=O group), 1741 (-COO- ester group), 2876 and 3070 (-C-H str. in -CH₃). **¹H NMR in δ (ppm)**: 0.90 (t, 9H, of -CH₃ in -OC₅H₁₁), 1.39 (m, 12H, n-poly methylene groups of -CH₂- in -OC₅H₁₁), 1.77 (m, 6H, -CH₂- in -OC₅H₁₁), 4.06 (t, 6H, -OCH₂- in -OC₅H₁₁), 7.11 (d, 6H, phenyl ring), 7.31 (s, 1H, phenyl ring), 7.73 (d, 1H, phenyl ring), 7.78 and 8.05 (d, 3H, phenyl ring), 8.13 (d, 4H, phenyl ring).

IR Spectra of Hexyloxy in cm⁻¹(E₂): **¹H NMR in δ (ppm)**: 0.89 (t, 9H, of -CH₃ in in -OC₅H₁₁ and -OC₆H₁₃), 1.38 (m, 16H, n-poly methylene groups of -CH₂- in -OC₅H₁₁ and -OC₆H₁₃), 1.79 (m, 6H, -CH₂- in -OC₅H₁₁ and -OC₆H₁₃), 4.06 (t, 6H, -OCH₂- in -OC₅H₁₁ and -OC₆H₁₃), 7.12 (d, 6H, phenyl ring), 7.31 (s, 1H, phenyl ring), 7.71 (d, 1H, phenyl ring), 7.78 and 8.06 (d, 3H, phenyl ring), 8.11 (d, 4H, phenyl ring).

3. Result and discussion

3.1 Mesomorphic behavior study

Herein, we have prepared newly λ -shaped azo-based liquid crystalline compounds with two linker groups joint by four phenyl rings and further substituted with a variable alkoxy side chain from a short alkyl chain (C₅) to a higher alkyl chain (C₁₈) at the right end side chain and a fixed pentyloxy (-OC₅H₁₁) tail group at the left terminal side. The esterification reaction of 4-n-alkyloxy benzoic acid (**A**) and 4-(4'-(pentyloxy) phenyl) diazenyl benzene-1, 3-diol (**D**) was carried out to form azo-ester based homologous series. The synthesized target compounds (**E**₁-**E**₈) were tested for the liquid crystalline properties on both heating and cooling cycle. Out of eight synthesized compounds in the present series, compound **E**₁ to **E**₈ shows enantiotropic nematic type mesophase whereas compound **E**₅ to **E**₈ exhibited enantiotropic smectic C phase with reduced mesophase thermal stability.

3.1.1 Polarizing optical microscopic study

The LC properties of newly synthesized materials were preliminary examined by using a polarizing optical microscope on both cooling and heating conditions. Further, the effect of variable alkoxy side chain on mesomorphic property has been studied and correlates with the previously reported homologous series. All synthesized eight compounds showed liquid crystalline properties on both heating and cooling conditions. Furthermore, comp. **E**₁ to **E**₈ displayed an enantiotropically type nematic mesophase, whereas compound **E**₅ to **E**₈ demonstrated a lamellar ordered type smectic C phase with the addition of nematic type mesogenic properties. It can be observed that the presence of liquid crystalline properties is mainly dependent on the molecular core, type of linking unit, polarity and polarizability throughout the molecular systems, flexibility of molecules caused by the number of side tail groups (-OR) on the terminal end⁴². The presence of linking groups on the molecular cores further affect their polarity, dipole moment, polarizability, and molecular interactions which is responsible for the liquid crystalline properties. On other hand, it can be noted that the single azo group based molecules are difficult to show any liquid crystalline properties, this is due to the formation *cis/trans* isomerization mixture which further destabilize the mesogenic properties. However, it shows excellent liquid crystalline properties when it is linked with some other supportive linking unit such as ester, Schiff-base, amide etc.⁴³. The phase behaviour of the observed transitions (SmC-I, Cr-N, N-I) curves in the present synthesized azo based series is shown in Figure 1. The transition temperature was steadily reduced as the series progressed from lower homologue (**E**₁) to higher homologue (**E**₈). Further, we have not observed any odd-even effect in the present synthesized series. The decreased van der Waals interactions between aromatic phenyl cores and the higher degree of flexibility due to the presence of a long alkyl chain in the alkoxy group at the left terminal section might explain the decreasing trend in melting and clearing temperature⁴³.

As can be seen from **Fig. 1**, the effect of higher alkoxy chain significantly affects the mesomorphic stability. Likewise, compound **E**₈ with octadecyloxy tail (-OC₁₈H₃₇) showed liquid crystalline properties at 52 °C on heating conditions. However, the liquid crystalline phase is stabilized upto 34 °C on cooling condition. The melting temperature decreases with the higher alkoxy-chain length, this may be due to the higher van der Waals association between the hydrophobic tails with an increase in the alkyl chain length. Further, we have compared our series (**E**₁-**E**₈) with structurally similar series. Ganatra et al. studied nonlinear azo-ester based series with terminal substituted -COCH₃ group and reported nematic type mesogenic properties⁴⁴. Later, Dixit et al. reported azo-ester based nonlinear series with electron withdrawing nitro group at terminal position and reported nematic and smectic C type mesogenic properties⁴⁵. Recently, Patel et al. reported electron donating groups (-CH₃, -OCH₃) based on two homologous series and reported monotropic smectic C and nematic types of LC properties⁴⁶.

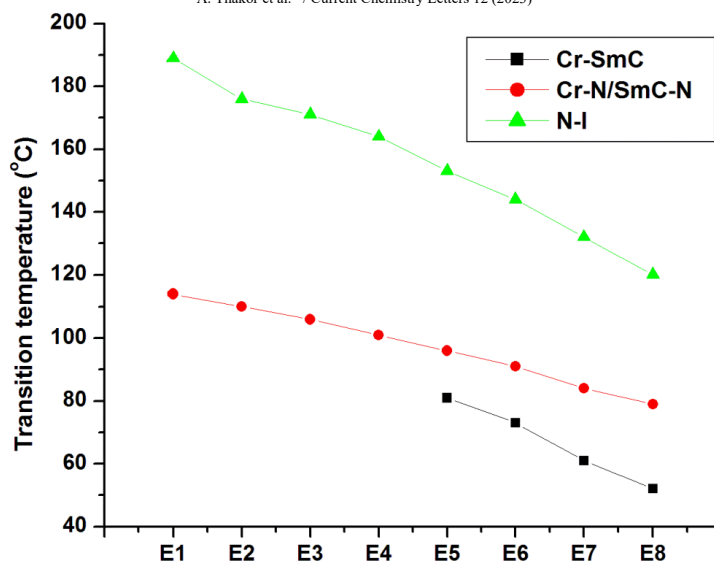


Fig. 1. Phase diagram of present series.

3.1.2 Textural study

For the microscopic study, the materials were heated to an isotropic condition on a transparent glass slide covered by a coverslip with the cooling rate of (2 °C/min). The texture images of the liquid crystalline state for the selected azo mesogens were shown in Fig. 2. Mostly synthesized compounds show schlieren and threaded type texture pattern of nematic phase while focal conic, needle, and broken focal conic type texture pattern for smectic C type mesophase. Compound E₈ showed broken fan type texture pattern of smectic C phase on 52.0 °C on heating while it transformed into nematic mesophase at 79.0 °C with schlieren type of texture pattern. It can also be reviewed on a cooling cycle where the phase appears at 76.0 °C for nematic and at 48.0 °C for smectic C phase. Similarly, compound E₇ with hexadecyloxy side group (-OC₁₆H₃₃) showed schlieren type texture pattern of nematic phase at 81.0 °C and on applying further cooling, it transforms into focal conic type texture pattern of smectic C phase at 59.0 °C on cooling cycle. The phase sequence of compound E₇ is recorded at different temperatures which clearly indicates the transformation of isotropic state to nematic mesophase, nematic mesophase to smectic C mesophase and smectic C to solid crystalline state respectively (Fig. 3). Fig. 4 represents the space-filling diagram of compound E₁ derivatives which clearly shows the nonlinear geometrical shape of the compound. Additionally, compounds with lower side alkyl spacer displayed nematic mesophase without showing any lamellar order type molecular arrangement which is responsible to form smectic type organization (Fig. 5). Compounds E₁, E₂, E₃ and E₄ showed nematic mesophase at 114.0 °C, 110.0 °C, 106.0 °C and 101.0 °C on heating and on further heating it transform into isotropic state at 189.0 °C, 176.0 °C, 171.0 °C and 164.0 °C respectively. All four derivatives showed an excellent mesophase temperature range of nematic mesophase.

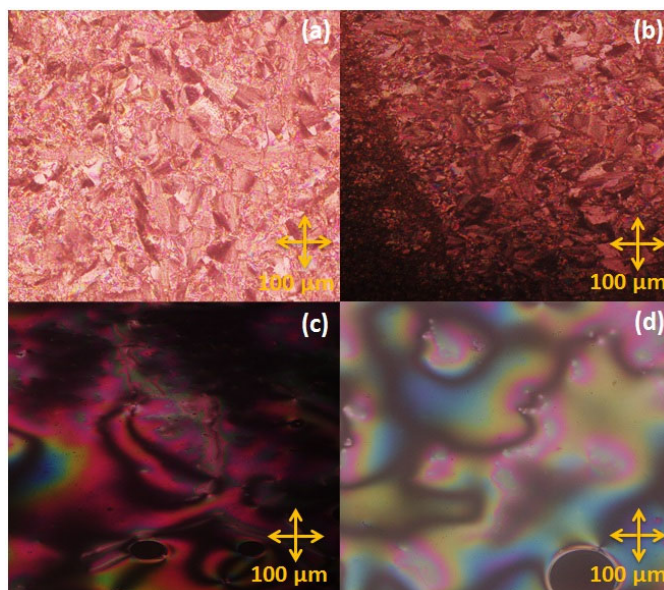


Fig. 2. Optical photomicrographs on cooling; (a) smectic C (comp.E₈) at 48.0 °C, (b) smectic C (comp.E₇) at 59.0 °C, (c) nematic (comp.E₄) at 97.0 °C, (d) nematic (comp.E₃) at 103.0 °C.

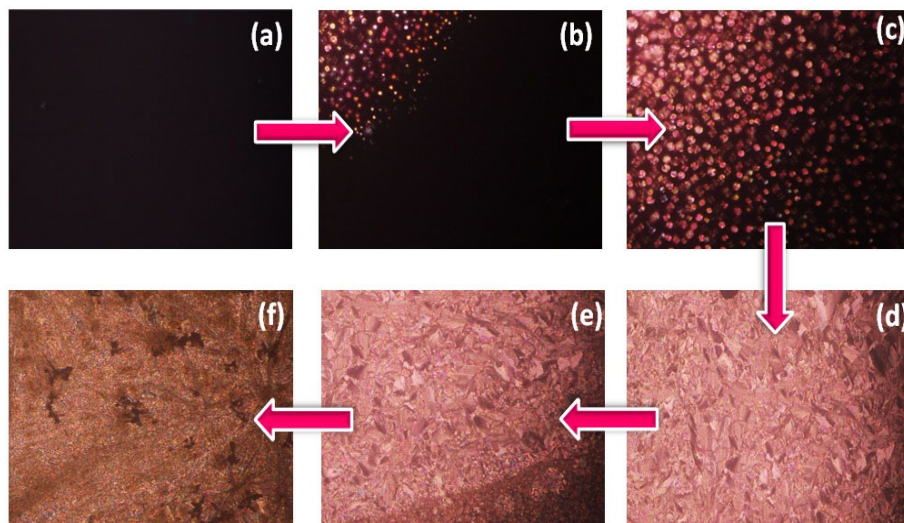


Fig. 3. Phase sequence of compound E7 on cooling condition, isotropic state at 132.0 °C(a), nematic droplets at 87.0 °C (b); nematic droplets at 69.0 °C (c), fan type texture (d), fan shape to solid transform (e), solid crystal at 24 °C (f).

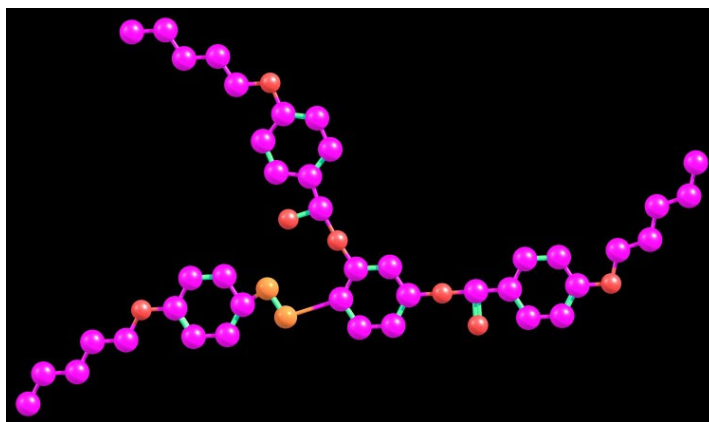


Fig. 4. Space filling diagram of λ -shaped compound E₁

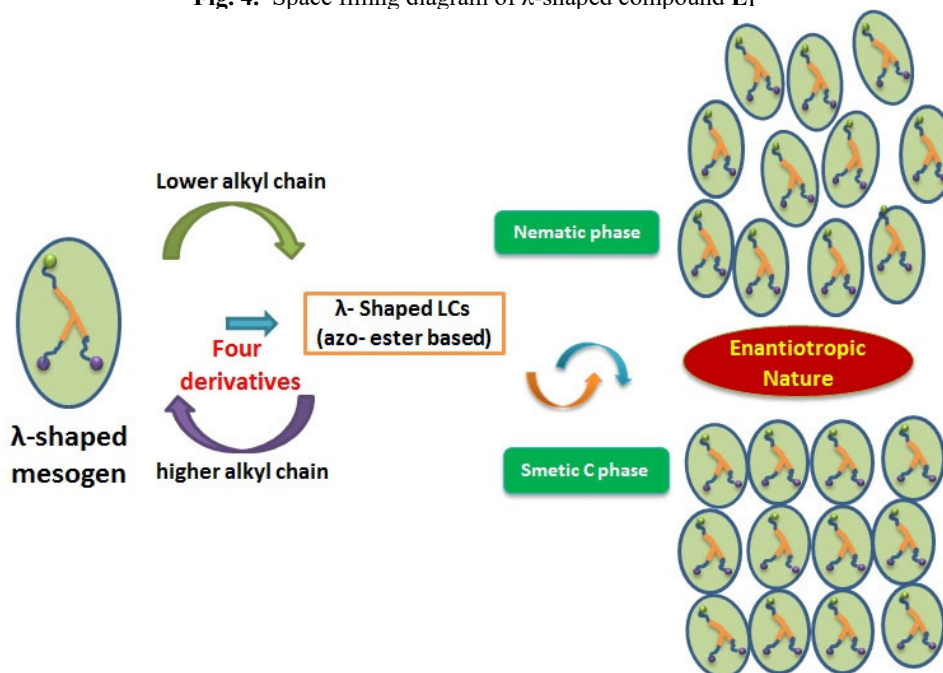


Fig. 5. Molecular arrangement in smectic C and nematic phase

3.2 Differential scanning calorimetry study

DSC measurements were used to determine the thermal behavior of new azo ester based homologous series, as illustrated in Fig. 6. All compounds showed endothermic peaks on both heating and cooling cycles. Compound E₁ with pentyloxy group (-OC₅H₁₁) showed two endothermic peaks at 112.8 °C and 189.1 °C corresponding to the presence of Cr-N and N-I phase transitions while on applying further cooling it again traced at 173.4 °C and 97.61 °C. It can be seen that the azo mesogens with short alkyl spacer showed higher enthalpy change (ΔH) value, which is commonly observed in liquid crystal phase transitions. Similarly, compound E₂ with hexyloxy group (-OC₆H₁₃) showed two endothermic peaks at 101.6 °C and 187.6 °C corresponding to solid to nematic and nematic to isotropic phase transition. This transition was again traced on cooling conditions respectively. Compound E₇ showed three endothermic peaks at 56.76 °C, 82.02 °C and 123.7 °C corresponding to the presence of Cr-SmC, SmC-N and N-I phase transitions, on applying cooling these transitions were again traced at 116.7 °C, 80.73 °C and 40.82 °C. Likewise, compound E₈ displayed three endothermic peaks at 49.83 °C, 76.73 °C and 124.8 °C on heating and on cooling it again observed at 118.3 °C, 67.20 °C and 34.97 °C respectively. It can be observed that the transition temperatures observed in DSC are quit nearer to POM temperatures. The transition temperatures, enthalpy change, and entropy change values are given in Table 2. A bar graph depicts the thermal behavior of selected mesogens from present synthesized azo based homologous series (Fig. 7). It also demonstrates that azo-ester linked mesogens displayed broad temperature range of mesophase, this may be due to the presence of a longer alkoxy chain which enhances the stability of molecules stacked in layered and side-by-side configurations and requires a higher temperature to construct the isotropic phase.

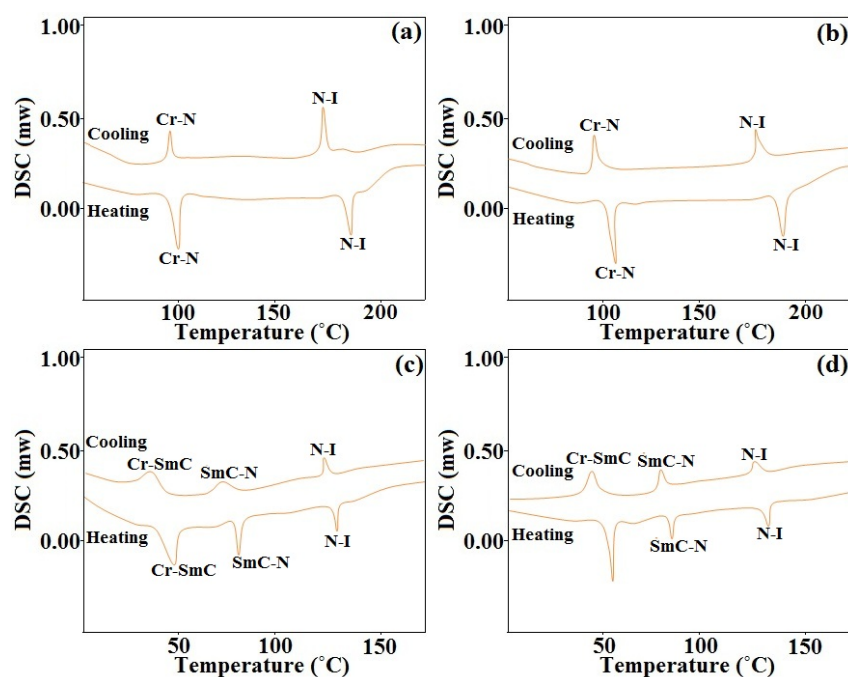


Fig. 6. DSC thermogram of compound (a) compound E₂; (b) compound E₁; (c) compound E₈; (d) compound E₇ on second heating and cooling cycle.

Table 2. Transition temperature (°C) of the azo based compounds by DSC measurement.

Comp.	Transition	Heating scan(°C)	Cooling scan(°C)	ΔH (J.g ⁻¹)	ΔH (J.g ⁻¹)	ΔS (J.g ⁻¹ .K ⁻¹)	ΔS (J.g ⁻¹ .K ⁻¹)
E ₁	Cr-N	112.8	97.61	34.2	23.5	0.088	0.063
	N-I	189.1	174.3	3.2	5.8	0.006	0.012
E ₂	Cr-N	101.6	98.23	25.7	20.6	0.068	0.055
	N-I	187.6	176.3	5.2	7.5	0.011	0.016
E ₃	Cr-N	104.5	101.7	32.8	15.7	0.087	0.041
	N-I	168.4	159.4	2.4	6.8	0.005	0.015
E ₇	Cr-SmC	56.76	40.82	22.5	18.6	0.068	0.059
	SmC-N	82.02	80.73	12.6	10.5	0.035	0.029
	N-I	123.7	116.7	1.5	6.8	0.003	0.017
E ₈	Cr-SmC	49.83	34.97	15.6	20.5	0.048	0.066
	SmC-N	76.73	67.20	10.5	10.4	0.030	0.030
	N-I	124.8	118.3	1.4	3.5	0.003	0.008

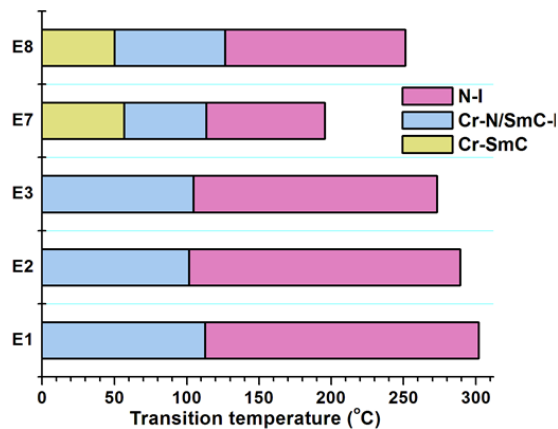


Fig. 7. Bargraph showing the thermal behavior of synthesized compounds from series

3.3 Thermal gravimetric analysis

The thermal stability of the synthesized azo mesogens was confirmed by using TGA analysis (Fig. 8). We have selected four derivatives for TGA analysis. All four azo based materials (E1–E4) displayed single-staged thermal decomposition. However, the azo-esters linked non-linear compounds with lower side spacer (E1, E2) displayed a different type of weight loss as compared to higher alkoxy side chain spacer (E3, E4). As compare to all mesogens, derivative E4 with decyloxy side group (-OC₁₀H₂₁) showed the highest weight loss of 73 % around 273–420 °C (Tmax = 362 °C) with the remaining residue completely decomposed around 650 °C. Further, compound E1, E2 and E3 with pentyloxy (-OC₅H₁₁), hexyloxy (-OC₆H₁₃) and octyloxy (-OC₈H₁₇) group showed 60-65 % weight loss around the temperature range between 320-375 °C with further complete degradation around 650 °C respectively. The decomposition is taking place due to the thermal cleavage of azo and ester groups with presence of periphery alkoxy side groups⁴⁷. These obtained results suggest the substitution of higher alkoxy side chains leads to higher weight loss as compared to lower chain substituted compounds.

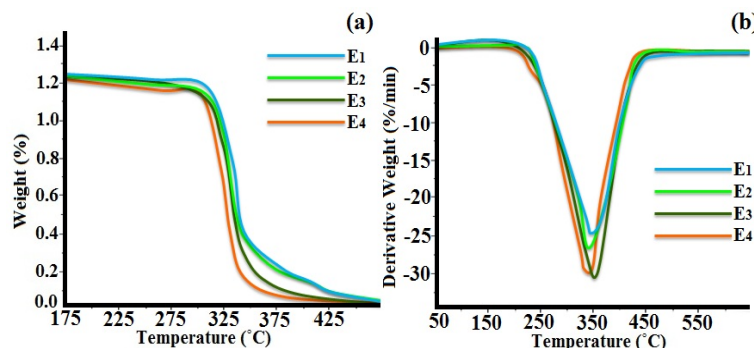


Fig. 8. (a) TGA and (b) DTG curves of compounds (E1–E4) at a heating rate of 20 °C/min under N₂ atmosphere

4. Conclusions

In this work, we have successfully designed and synthesized newly λ -shaped homologous series based on azo-ester linking group and different alkoxy groups as terminal side positions and further well characterized by using various spectroscopic techniques. Further, we have studied the effect of terminally substituted variable alkoxy side groups (-OR) at the two different positions on the azo-ester core based molecules and studied its effect on the mesomorphic properties to understand the structure-property relationship. All synthesized eight azo mesogens exhibited enantiotropical type nematic and smectic C type mesophase. The TGA analysis confirmed the thermal stability of the synthesized compounds is relatively high as above to 320 °C. The lower alkoxy side chain substituted compounds showed only nematic type mesophase while higher alkoxy chain substituted compounds displayed smectic C and nematic phase.

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