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Synthesis and study of mesomorphic properties of azoester compounds

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ABSTRACT

In order to investigate the influence of the terminal substitution on mesomorphism, the newly synthesized homologues series based on azoester have been synthesized. The influence of the structure of the mesogenic core has been present in this study, effect of hydrocarbon chain length and flexibility at terminal side effect on mesomorphism was represents in this case. In this investigation, we represent a series consisting of thirteen (C_1–C_{18}) homologue. In which, C_1 to C_3 homologue are nonmesomorphic. While C_4–C_{18} shows smectic as well as nematic mesophase enantiotropically. Analytical and spectral data confirmed the molecular structures of homologues. All these compounds were characterized by elemental analysis and Fourier transform infrared [FTIR] and ^{1}H NMR. Their mesomorphic properties were measured by optical polarized light microscopy and differential scanning calorimetry (DSC) and PXRD.

KEYWORDS

Mesophase; nematic; smectic; azoester

Introduction

The mesomorphic behavior of an organic compound is generally dependent on its molecular shape in which a slight change in the molecular geometry brings about considerable change in its mesomorphic properties. The study on azoester-based liquid crystalline material (LC) is an important due to their applications and usefulness in the benefit of mankind. Liquid crystalline material (LCs) have shown a properties between those of a conventional liquid and a solid crystal, and their applications are widespread, LC displays to lasers, photovoltaic, nonlinear optics to switchable windows and sensors, etc. [1–3]. The number of azoester homologous series of mesogens were reported earlier with a view to understand the effect of structure on mesomorphic properties in various fields like manufacture of electronic display devices (LCD), e.g., screen of television, electronic curtains, medical field to manufacture of thermographic articles [4–8]. In this following status, we planned to synthesize a newly LC material through homologous series. In present series, the molecular rigidity is altered by additional linking of the central group –N=N- (azo) to the ester linking group and the flexibility is altered and also effected by terminal side chain. The LC properties and behaviors will be compared with structurally similar other series reported in literature. The group efficiency order will be derived from thermal stability, degree of mesomorphism and the commencement of mesophase. Doshi et al. have previously reported that a azoester linking base calamatic liquid

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Table 1. Elemental Analysis for (1) Pentoxy, (2) Hexoxy, (3) Heptoxy, (4) Octyloxy, and (5) Dodecyloxy derivatives.

		Elements % found			Elements % calculated		
Sr. No.	Molecular formula	C	H	N	C	H	N
1	$C_{29}H_{34}O_4N_2$	73.21	7.1	5.86	73.41	7.17	5.9
2	$C_{30}H_{36}O_4N_2$	73.72	7.31	5.68	73.77	7.37	5.73
3	$C_{31}H_{38}O_4N_2$	74.05	7.5	5.53	74.1	7.56	5.57
4	$C_{32}H_{40}O_4N_2$	74.35	7.68	5.39	74.41	7.75	5.42
5	$C_{36}H_{48}O_4N_2$	75.46	8.32	4.8	75.52	8.39	4.89

crystal through three phenyl rings and study the stability of smectic to nematic to isotropic phase [9–12].

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated using suitable alkylating agent(R–X) to convert it into 4-*n*-alkoxy benzoic acids(A) method modified by Dave and Vora co-workers[13], the alkylation of Paracetamol using alkylating agent *n*-$C_5H_{11}Br$ is synthesized to form 4-*n*-pentyloxy acetanilide, which on hydrolysis converted to 4-*n*-pentyloxy aniline is form by usual establish method. Azo dye (B) 4-hydroxy phenyl azo 4′- Pentyloxy benzene (m.p. 116°C, yield 75%) was prepared by azotization method. Final azoester products were synthesized by condensation of (A) and (B) [14]. Thus, the azoester homolog derivatives were filtered, washed with sodium bicarbonate solution followed by distilled water, dried, and purified till constant transition temperatures obtained using an optical polarizing microscope equipped with a heating stage. 4-hydroxy benzoic acid, Alkyl halides, Paracetamol, dicyclohexyl carbodimide (DCC), Dimethyl amino pyridine (DMAP), DCM, MeOH, Acetone required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic path of this series is represents in Scheme 1.

Characterization

The representative homologs of a series were characterized by general elemental analysis, infrared spectroscopy, ^{1}H NMR spectra, IR spectra were recorded on Perkin-Elmer spectrum GX,^{1}H NMR spectra were recorded on Bruker using $CDCl_3$ as solvent. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyzer (Table 1). Transition temperature and LC properties (textures) were determined using an optical polarizing microscopy equipped with heating stage (POM). All texture images of nematic phase were determined by miscibility method (Table 2). The decomposition temperatures were determined using a Shimadzu DSC

Table 2. Texture of Nematic Phase of C5, C7, C14, C16 by miscibility method.

Sr. No.	Homolog	Texture
1	C_5	Schlieren
2	C_7	Threaded
3	C_{14}	Schlieren
4	C_{16}	Nematic droplets

Table 3. Transition temperature of series 1: 4-*n*-alkoxy benzoyloxy-phenyl azo-4″-pentoxy benzene.

Compoud No	*n*-alkyl chain C_nH_{2n+1}	Transition Temperatures in(°C)		
		Smectic	Nematic	Isotropic
1	C_1	—	—	150.0
2	C_2	—	—	145.0
3	C_3	102.0	126	140.0
4	C_4	92.0	106.0	130.0
5	C_5	78.0	88.0	127.0
6	C_6	87.0	98.0	126.0
7	C_7	82.0	92.0	118.0
8	C_8	80.0	102.0	116.0
9	C_{10}	81.0	104.0	127.0
10	C_{12}	74.0	90.0	108.0
11	C_{14}	71.0	88.0	104.0
12	C_{16}	69.0	84.0	100.0
13	C_{18}	57.0	71.0	87.0

60 differential scanning calorimeter with a heating rate of 10.0°C min^{-1} in air. X-ray diffraction (XRD) experiments were performed on a X'PERT MPD, using Cu Kα X-ray lines at 40 kV and 30 mA. The XRD patterns were recorded at transition temperature of compounds.

Synthesis route

IR Spectra (KBr) in cm−1 for hexaloxy, dodecyloxy derivatives

Hexaloxy: 761 Poly methylene (-CH2-)n of –OC6H13, 885(–C-H- def. di-substituted-Para), 690 Polymethylene (-CH2-) of –OC5H11, 989 (—C-H- def. hydrocarbon), 1060 and 1105(-C-O-) Str, 1296 and 1321 and 1423, 1494 (-C-O str in –(CH2)n chain), 1579 (-C-H- def. in CH2), 1390 (-N=N-)str, 1641 (-C=O group), 1735 (-COO- ester group), 2870 and 3072 and (-C-H str in CH3).

Dodecyloxy: 759 and 796 Polymethylene (-CH2-)n of –OC12H25, 883(–C-H- def. m di-substituted-Para), 989 (—C-H- def. hydrocarbon), 1008, 1056, (-C-O-) Str, of -OC5H11, 1276 and 1392 and 1373, 1246(-C-O str in –(CH2)n chain, 1496(-C-H- def. in CH2),1512 and 1392 (-N=N-)str, 1598 (-C=O group), 1737 (-COO- ester group), 2733 and 2916 and 3084 (-C-H str in CH3).

1H NMR spectra in CDCl3 in δ ppm for tetradecyloxy and octyloxy derivative

Tetradecyloxy: 0.89(t, -CH2-CH3, 4 H), 1.26 (m, n-poly methylene groups of –OC14H29), 1.31–p1.76(q, -CH2-CH3, 6 H), 1.76(m, 8 H of poly methylene group), 3.98(t,-OCH2-CH2-, 4 H), 7.19 and 7.83(s, ArH, p-disubstituted),8.07–8.19(s, ArH, p-di substituted phenyl ring).

Octyloxy: 0.88–0.89(t, -CH2-CH3, 4 H, of –C6H13 and -C8H17), 1.29(m, n-poly methylene groups of -OC8H17), 1.76(m, 8 H of polymethylene), 4.06 (t, 4 H, -OCH2-CH2-of -OC6H13 and -OC8H17), 7.18–7,57 (s, ArH, substituted benzene), 8.07–8.11 (s, ArH, p-substituted phenyl ring).

Result and discussion

The 4-hydroxy azo-4″-pentoxy benzene (m.p. 116°C, yield 75%) is a linear in shape, but non-LC dyes. However, it is linking with dimerised 4-*n*-alkoxy benzoic acid. It is interestingly shown that its shows liquid crystalline property (C_3–C_{18}) and non mesomorphic (C_1, C_2) homolog, respectively. In this study, we have prepared homologs series that display mesophase

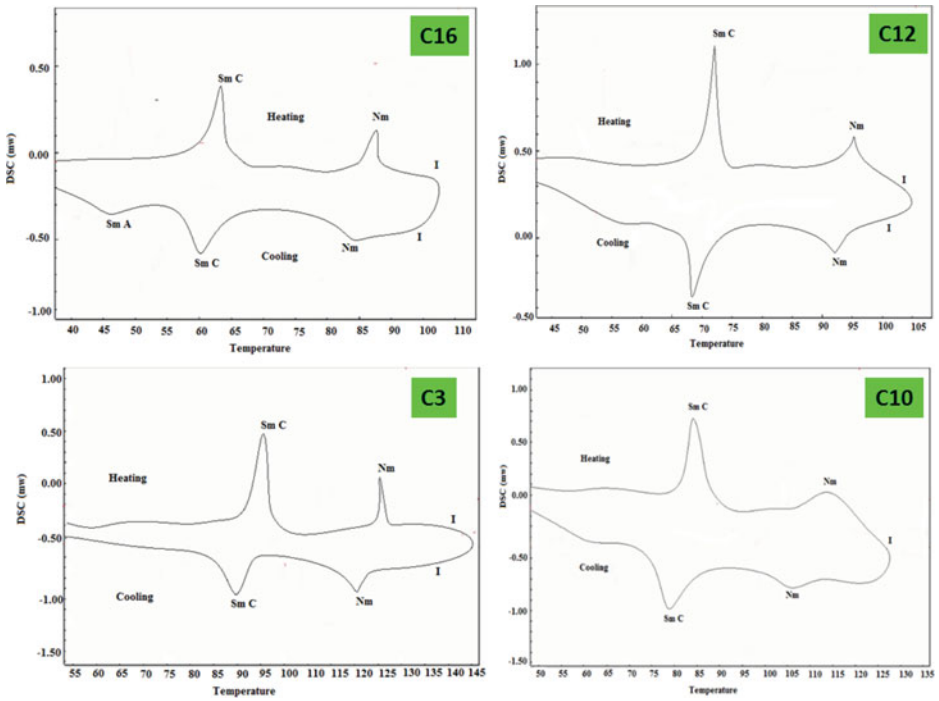

Figure 1. DSC behaviour of comp. C16, C12, C3, C10 at heating and cooling condition.

at lower transition temperature. The LC homologs are enantiotropically smectogenic and nematogenic manner, respectively.

The transition temperatures of novel synthesized homologs series are lower as compared to the dimerised *n*-alkoxy benzoic acid. The transition obtain from the solid state to mesomorphic is directly as associated with the melting point. The thermal and liquid crystalline behavior of these compounds was investigated by using a combination of differential scanning calorimetry (DSC) and polarization optical microscope equipped with heating stage (POM). During the ordering sequence of mesophase at two endothermic and exothermic peaks at heating and cooling stage, two peaks are obtained starting peak associated with solid to mesomorphic transition temperature, and large peak at high temperature shows liquid transition phase, respectively. The isotropic temperature is detected by the POM images. Figure 1 shows the DSC results of comp. C_{16}, C_{12}, C_3, C_{10}. The thermogram shows that firstly an endothermic peak observed at 62°C (C_{16}), 71°C (C_{12}), 96°C (C_3), 85°C (C_{10}). The corresponding change in the enthalpy (ΔH) was observed approximately 58.0 J/g (C_3), 53.0 J/g (C_{10}), 41.6 J/g (C_{12}), 34.1 J/g (C_{16}). While, the second endothermic peak occurred at 123°C (C_3), 114°C (C_{10}), 95°C (C_{12}), 86°C (C_{16}) and the enthalpy change (ΔH) was obtained at 12.8 J/g (C_3), 8.8 J/g (C_{10}), 8.2 J/g (C_{12}), 9.2 J/g (C_{16}). However, during the cooling stage, two consecutive exothermic peaks were observed, in the following compound C_3 at 88°C and 118°C, for compound C_{10} shown two peaks observed at 77°C and 105°C, while comp. C_{12} at cooling condition the peaks observed at 67 and 93°C, respectively. The mesophase is confirmed by the POM.

From the POM study, we confirm that the mesophase observed in present synthesized homologs series. The phase diagram is plotted against number of carbons atoms present in left alkoxy terminal group (-OR). The phase diagram consisting of Cr-M/I, Sm-N, and N-I transition curve is obtained by linking the transition temperature points, phase behaviors of a novel

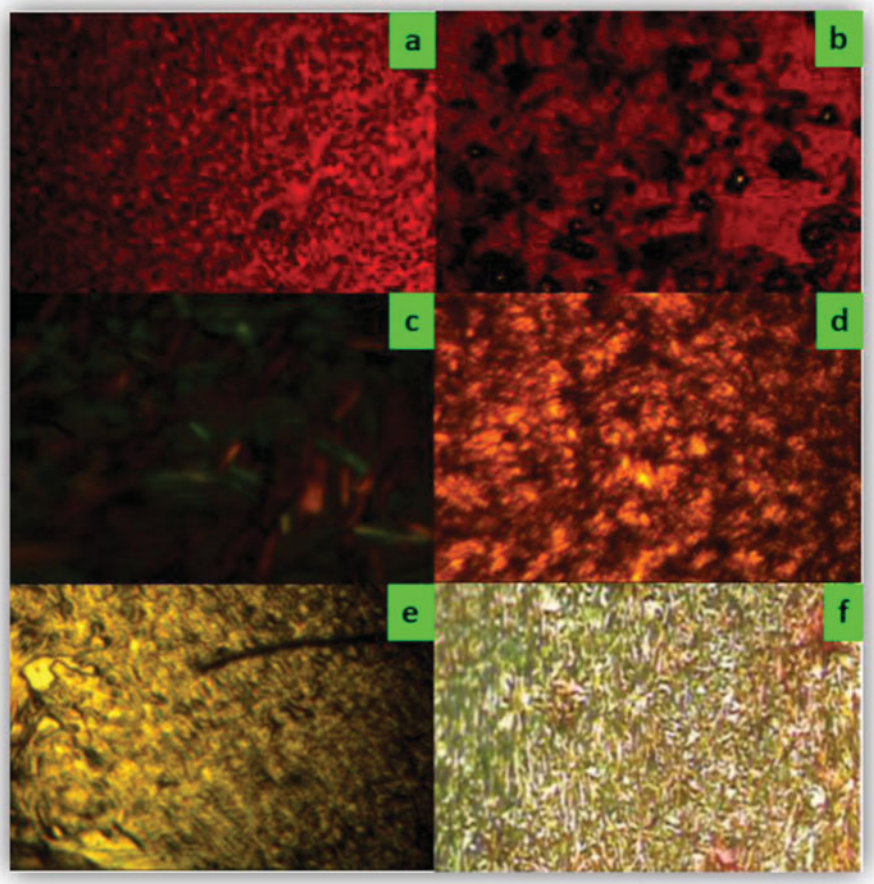

Figure 2. POM image (a) Sm C phase at 92°C of comp. C4 (b) Sm A phase at 88°C of comp. C5 (c) Sm A phase at 69°C of comp. C16 (d) Nematic phase at 92°C of comp. C7 (e) Nematic phase at 90°C of comp. C10 (f) Sm C phase at 80°C of comp. C8.

series as shown in Fig. 3. The Cr-M/I transition curve follows a zigzag path and behaved like rising and falling with overall descending tendency and behaved just like in normal manner. The Sm-N transition initially descends and rises maxima at C_6 homolog and then descends at C_8 homolog and rises to C_{10} and descends upto C_{18} homolog, which also exhibits the odd-even effect from C_5–C_7 homolog respectively. An N-I transition curve descends initially at C_5 homolog, due to the abnormality and rises from C_6 homolog to maxima at C_{10} homolog and then descends as series is ascends up to C_{18} homolog with exhibition of odd-even effect from C_5–C_7 derivative. The odd-even effect is shown from for C_5–C_7 homolog in N-I curve and then disappear for higher homologs for longer *n*-alkyl chain at left *n*-alkoxy terminal group. Sm-N transition and N-I transition curve is extrapolated to C_2 homolog to determine the absence of smectogenic character in C_2 homolog, respectively. C_1 and C_2 materials displays non-LC property due to high crystalline tendency to directly converted in to isotropic liquid without show any kind of mesomorphism [15–20].

In Fig. 2, comp. C_4 exhibits needle type of smectic C phase observed at 92°C during the heating condition, comp. C_5 shows broken focal-conic phase at 88°C in enantiotropically manner, comp. C_{16} shows fan-like smectic A phase, comp. C_7 shows nematic phase at 92°C at

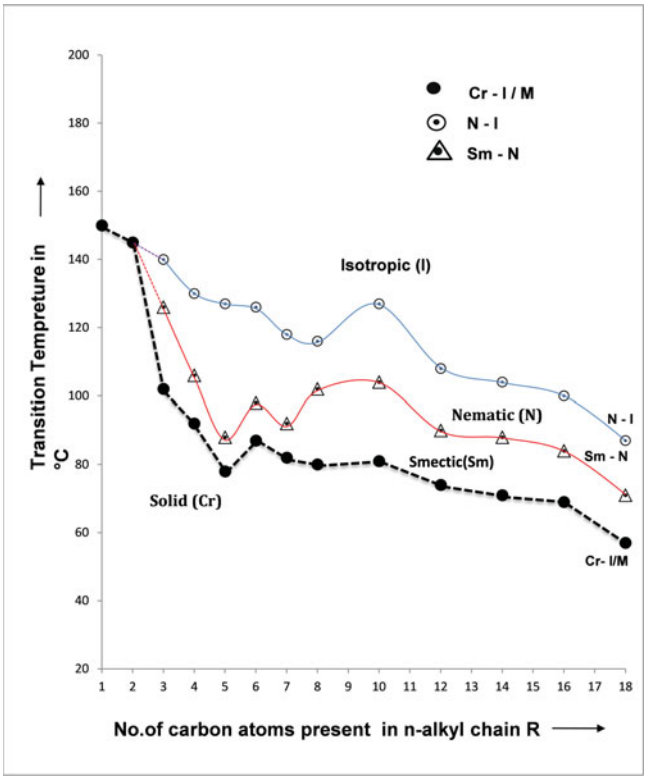

Figure 3. Phase diagram of series1.

heating and cooling condition, comp. C_{10} shows nematic droplets at 90°C at heating condition. However, C_8 homolog shows needle type phase of smectic C phase, respectively. Nematic phase were also determined by miscibility method given Table 2 and shows threaded type image.

Thermal stability for smectic is observed at 95.3 and mesophase length or the degree of mesomorphism vary from 10 to 24°C at the C_7 and C_3 homologs, respectively. However, for the nematic phase 121.8 and mesophase length 30–49°C at C_3 and C_{18} homologs. Mesomorphic properties of present series varies from homolog to homolog keeping right terminal side ($-OC_5H_{11}$) constant and varying left alkoxy side chain. The exhibition of smectogenic character from C_3 to C_{18} homolog is attributed due to formation of lamellar packing of molecules in the crystal lattices of rigid crystals which uphold sliding layered molecular arrangement in fluctuating condition under the influence of exposed thermal vibrations, which confirms the present of smectic character in enantiotropically manner. In order to correlate the results of the DSC and POM, we performed X-ray diffraction to confirm the highly ordered smectic phase in the compounds. We performed XRD for C_{12} and C_{14} homolog. The XRD pattern of compound C_{12}, which was carried out at nearly transition temperature 68°C, shown in Fig. 4. Low angle broad peak at ($2\theta = 3–5''$), and mid angle region at ($2\theta = 6–8''$) d-spacing of the reflections observed at 8.2 and 8.2 and 1.3, while compound C_{14}, ($2\theta = 3–4.8''$) and second significant peak at ($2\theta = 8.2–9.4''$). No any other significant peaks observed at higher angles in present series. Due to the longer chain at alkoxy side chain and linearity of molecule with azo (-N=N-) as a central linkage which also increases the stability of smectic phase. The reflections for the small angle area indicate the presence of smectic phase.

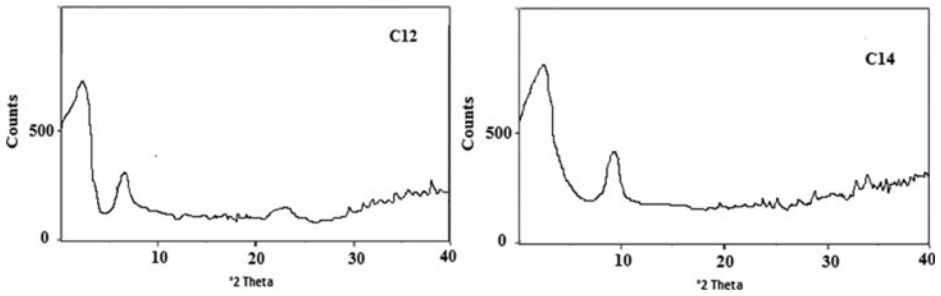

Figure 4. XRD traces of compounds C12, C14 measured at 68°C.

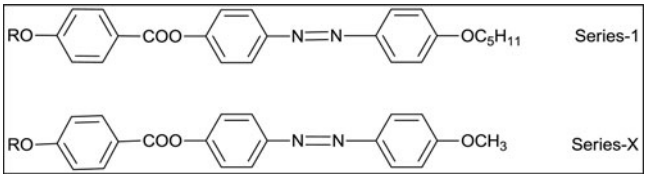

Figure 5. Structurally similar series.

Nonmesogenic homologs (C_1, C_2) sharply and directly transform into isotropic state during the cooling conditions. The same materials solidifies in rigid crystalline state arises due to their high crystalline tendency arising from low dispersion forces and low dipole-dipole interactions into convert directly into isotropic liquid without show any kind of mesomorphism and as results of unfavorable combined effect of molecular rigidity and flexibility. In the absence of mesomorphism in C_1 and C_2 homologs due to present of shorter *n*-alkyl side chain in alkoxy chain. Average middle-ordered thermal stability 121.38 of nematogenic mesophase is due to the lowering of N-I transition by breaking of hydrogen bonding from dimerised *n*-alkoxy benzoic acid. The deviations in mesomorphic properties is attributed by the changing number of methylene unit in left –OR flexible part group, keeping right terminal constant operates azoester based homologs series. The LC properties of present novel series-1 were compared with structurally similar series X as mentioned below Fig. 5, to study the effect of terminal group effect on mesomorphism. Series 1 and X have similar in the shape and three phenyl benzene core with similar linkage groups –COO- and –N=N- and differing at terminal side chain. Series X contain Methoxy (-OCH_3) at right terminal that keeps shorter length, while in series 1 at terminal side Pentoxy (-OC_5H_{11} (n) / –O-CH_2-CH_2-CH_2-CH_2-CH_3) or –CH_3 polar groups; variations in series to series is increased at side chain increased in hydrocarbon chain and effect on the mesophase caused by increasing in the flexibility of the molecular structure and that instigates lower thermal stability as compare to series X [21].

Thermal stability of smectic-nematic or smectic-isotropic stability previously reported [X]137.0 (C_{14}–C_{16}) and commencement at C_{14} homolog, while in present series 1, thermal stability of smectic to nematic is 95.3 (C_3–C_{18}) and commencement at C_3 homolog, respectively. The stability of nematic-isotropic in series X is 251.7 (C_1–C_{14}), for series 1 is 121.8. Thermal stability of nematic to isotropic is less in series 1 as compared to series X, due to the effect of terminal short chain that causes molecular vibrations at higher temperature [22]. The molecular rigidity due to phenyl ring and linking of central linkage with same series. Figure 6 represents the geometrical shape of present series 1 and structurally similar series that is taking with comparison series X.

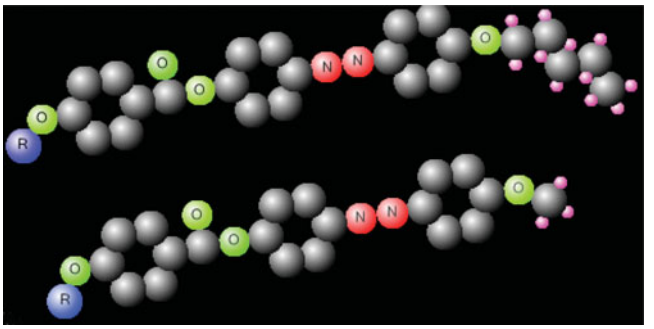

Figure 6. Space filling diagram of series 1 and series X.

The exhibition of nematogenic character by two azoester-based homologs series is attributed in presence of benzene core unit with –COO- and –N=N- linkage unit. Thermal stability of nematic to isotropic phase is lower in series 1 as compared to series X. The thermal stability normally depends upon the resistivity offered by homolog or homologs of a certain series constituting enthalpy change (ΔH) value which is allied with magnitudes resistivity of the revealed thermal vibrations to accelerate molecular arrangement in floating condition maintaining smectic or nematic phase. In present series 1, terminal group ($-OC_5H_{11}$) / $-O-CH_2-CH_2-CH_2-CH_2-CH_3$ bearing etherial linkage through the third phenyl ring to facilitate smectic mesomorphism, respectively.

Conclusions

In summary, we have synthesized successfully a newly series with contain two linking groups, which shown exhibits partly smectogenic and predominantly nematogenic with low ordered melting type. The textures examined focal conic, needle shape, threaded, schlieren images. The mesogenic property of homolog was confirmed by DSC and POM. Smectic phase was confirmed by XRD measurement at their transition temperatures. The present homologs series appearances low-ordered melting type of mesophase, which can be transported to low as 20–25°C to study of binary systems.

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