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Synthesis, Characterization and Investigation of Side Chain Length and/or Substituents Effect on the Liquid Crystal Properties of New Mesogens

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New substituted and unsubstituted phenol based mesogene series having an azo central linkage was synthesized by fixing phenol as rigid core unit with aromatic amine. The terminal –OH group was esterified successively by long alkyl chain acid chloride of variable length (n = 2, 6, 11, 15, 17). All 25 synthesized compounds exhibit mesomorphism. The effect of side chain length and substituents on the stability of liquid crystals was studied. The study reveals that nitro substituent destabilizes nematic and smectic phases more than floro substituent. Furthermore, the transition temperature decreases as the length of side chain increases.

Keywords liquid crystal, azo linkage, diazotization, phenol, aromatic amines

Introduction

The liquid crystals field has been inspiring scientists ever since its discovery in 1880 (1). The synthetic chemists involved in designing the unique structural features of liquid crystals and physicists are busy in exploring the new possible horizons of their applications (2). The quest to have better liquid crystals with a wide range of applications stimulated scientists to unveil the hidden and complex facts of various transition phases of liquid crystal molecules (3). It resulted in the discovery of new liquid crystals including chiral (4), ferroelectric and anti ferroelectric (5) compounds. Liquid crystalline phenomena are observed in a wide range of areas in the physical and biological sciences (2), ranging from such obvious technological applications (6) as the twisted nematic and ferroelectric display devices (7), and the widespread use of surfactants in the cleaning industry (8), through to the importance of self-assembly in a large number of biological processes (6), mesogenic behavior is clearly a topic worthy of investigation.

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Until 1983, it was thought that anything which sticks out at the side of a molecule disrupts molecular packing and diminishs the liquid crystal stability (9) as found by Jákli and coworkers (7). Surprisingly, compounds with lateral flexible substituents exhibit liquid crystalline phases. Later on, subsequent research revealed that disruption to the molecular packing due to lateral substituents is particularly advantageous for the mesomorphic and physical properties required for applications (10). A large number of work is reported by Weissflog et al. (11), Jákli and Saupe (12), Jákli (13) on mesogens with lateral aromatic substituents. Subsequent studies reported by Beresnev et al. (14), Perez et al. (15), Berdague et al. (16), Weissflog et al. (17), Berdague et al. (18) revealed that substituents are important in both nematic and smectic systems, although they reduce smectic phase stability (especially more ordered smectic phases) more than nematic phase stability (19).

Terminal groups are virtually always employed in the liquid crystal system (20). They give flexibility to the rigid core structure and tend to reduce melting points and allow liquid crystal phases to exhibit by stabilizing the molecular orientations necessary for liquid phase generation. The length of terminal group is crucial in generating mesogenic properties (21).

Diazo compounds are known to have excellent mesomorphic properties compared with the corresponding ester ones (22). The azo linkage is quite stable and directs the molecules to adopt peculiar shape suitable for liquid crystals behavior (23).

Compounds with central diazo linkage are of interest in electro-optical applications as wide range nematic materials having a large optical birefringence and a low viscosity (24).

They also find applications in the fields of photonics and optical information storage (25). The high dipole moment due to azo linkage and appropriate substituents provide strong photoinduced birefringence (26), and this property makes their utility in NLO application (27).

In the present work, we have synthesized four series, including unsubstituted and substituted azo mesogens with floro and nitro as leteral, and methoxy as para substituents with varing side chain length, in order to study substituents effect and length of side chain on the mesomorphic properties and transition temperatures. The lateral substituents (floro/nitro) were introduced to investigate the thermal stability of synthesized liquid crystal compounds.

Experimental

Characterization

Microanalysis of the compounds were performed on a Coleman Carbon-Hydrogen analyzer, and IR spectra were recorded on Perkin-Elmer 1605 FTIR spectrometer, using KBr pellets. The calorimetric studies were carried out on a Perkin-Elmer DCS 7 apparatus by adopting a scanning rate of 2.0°C/min. UV-Vis Spectra were obtained on a Shimadzu 160A UV-Vis recording spectrophotometer.

The ^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometer in $CDCl_3$ using TMS as internal standard. Liquid crystalline properties were investigated on a Leitz Labourlux 12 POL microscope provided with a heating stage. Melting points were determined on a Gallenkamp apparatus in a sealed capillary. Analytical TLC performed on precoated silica gel plates (SiO_2, Merck PF 254), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for column chromatography.

p-Toluidine, thionyl chloride, propanoic acid, heptanoic acid, lauric acid, hexadecanoic acid, octadecanoic acid, phenol(BDH), aniline, nitroaniline, floroaniline (fluka) were used as received. Tetrahydrofuran was dried by refluxing over sodium/benzophenone, then fractionally distilled and stored over molecular sieves. All other solvents were dried and distilled prior to use. The compounds were prepared according to the following Schemes 1–2.

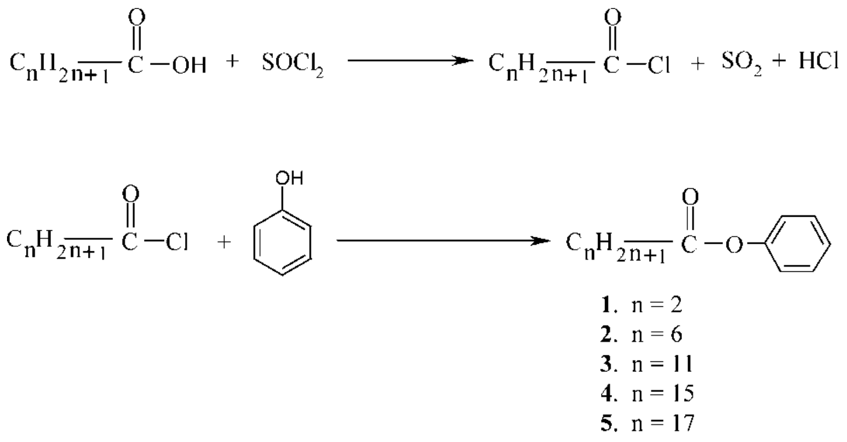
A General Procedure for the Synthesis of Phenyl Alkanoates (28)

Carboxylic acids of variable side chain length (n = 2, 6, 11, 15, 17) were taken in 100 mL two-neck round bottomed flask and was gradually heated to 50°C. Dry thionyl chloride (1.6 mol) in excess was added slowly while stirring, and then this mixture was refluxed for about 30–40 min at 70°C by adding 2–3 drops of DMF. The excess thionyl chloride was removed by repeated evaporation in vacuum. The crude acid chlorides were then purified by vacuum distillation.

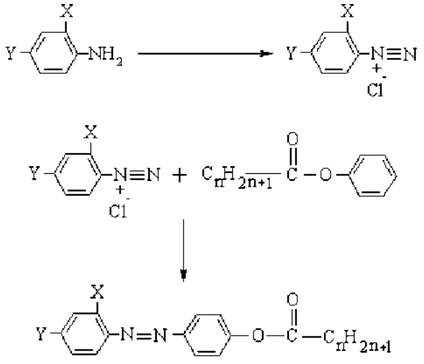
These acid chlorides were subsequently allowed to react with phenol in dry THF in the presence of NaH while stirring for 1 h at room temperature. Finally, 30 mL of water was added slowly to the mixture and stirred further for 10 min. The corresponding esters were extracted in chloroform, washed with distilled water and dried by anhydrous sodium sulphate. The chloroform was evaporated and esters were recrystallized from ethanol (27).

Phenyl Propanoate (1)

The procedure is listed above and the yield was 72%, oily liquid UV Phenol: 273 (0.765) 216 (0.710) Phenyl propanoate: 264 (0.673), IR (KBr) 1742 cm^{-1} (C=O), 1508 cm^{-1} (Aromatic C=C). Anal. calcd. for $C_9H_{10}O_2$: C, 71.98%; H, 6.71%; O, 21.31%. Found: C, 70.89%; H 6.28% O, 20.98%.



Scheme 1. Synthesis of aliphatic acid chlorides and phenol based aromatic esters with varying degrees of side chain length.



		a	b	c	d	e
6. X=H,	Y=H	n=2	6	11	15	17
7. X=NO$_2$	Y=H	n=2	6	11	15	17
8. X=F,	Y=H	n=2	6	11	15	17
9. X=H,	Y=OCH$_3$	n=2	6	11	15	17

Scheme 2. Synthesis of substituted and unsubstituted phenol based mesogene series having an azo central linkage.

Phenyl Heptanoate (2)

The procedure is listed above and the yield was 74%, oily liquid, UV Phenol: 273 (0.765) 216 (0.710) Phenyl propanoate: 262 (0.645), IR (KBr) 1751 cm^{-1} (C=O), 1576 cm^{-1} (Aromatic C=C). Anal. calcd. for $C_{13}H_{18}O_2$: C, 75.69%; H, 8.80%; O, 15.51%. Found: C, 74.99%; H, 8.37% O, 14.98%.

Phenyl Dodecanoate (3)

The procedure is listed above and the yield was 77%, oily liquid, UV Phenol: 273 (0.765) 216 (0.710) Phenyl propanoate: 261 (0.689), IR (KBr) 1748 cm^{-1} (C=O), 1553 cm^{-1} (Aromatic C=C). Anal. calcd. for $C_{18}H_{28}O_2$: C, 78.21%; H,10.21%; O, 11.58%. Found: C, 78.10%; H, 9.97% O, 11.16%.

Phenyl Hexadecanoate (4)

The procedure is listed above and the yield was 81%, m.p 58°C, UV Phenol: 273 (0.765) 216 (0.710) Phenyl propanoate: 260 (0.663), IR (KBr) 1757 cm^{-1} (C=O), 1593 cm^{-1} (Aromatic C=C). Anal. calcd. for $C_{22}H_{36}O_2$: C, 79.46%; H,10.91%; O, 9.62%. Found: C, 78.90%; H, 10.07% O, 9.26%.

Phenyl Octadecanoate (5)

The procedure is listed above, and the yield was 83%, m.p 78°C, UV Phenol: 273 (0.765) 216 (0.710) Phenyl propanoate: 264 (0.673), IR (KBr) 1748 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C). Anal. calcd. for $C_{24}H_{40}O_2$: C, 79.94%; H,11.18%; O, 8.87%. Found: C, 79.10%; H, 10.77% O, 8.20%.

A General Procedure for the Synthesis of Substituted and Unsubstituted 4-(phenyldiazenyl)phenylalkanoate

Aromatic amines (aniline, *o*-nitroaniline, *p*-ansidine, *o*-floro aniline) were suspended in a stirred solution of 2N HCl (16 mL) and 6 mL water. To this mixture, a solution of sodium nitrite in water (10 mL) was added slowly. During this addition, the temperature was maintained at −10°C to −5°C using ice salt mixture. The whole mixture was then stirred for 5 min. The corresponding ester was added slowly with stirring while keeping the temperature −5°C to −2°C for 1 h. It was further stirred at room temperature for 2 h, and then 1 h more by adding NaOAc (20 g in 20 mL water). The precipitated was collected by filtration, washed with water, and finally purified on a silica gel column with methanol and dichlromethane (1 : 3) as eluent to afford pure product (29, 30).

Unsubstituted Phenol Based Azo Mesogens

4-(Phenyldiazenyl)phenylpropanoate [6a]. The procedure is described above, and the yield was 82%, IR (KBr) 1744 cm^{-1} (C=O), 1586 cm^{-1} (aromatic C=C), 1590 cm^{-1} (N=N) Anal. calcd. for $C_{15}H_{12}N_2O_2$: C 70.85%; H 5.55%; N 11.02%., O 12.58%. Found: C 70.11%; H 5.48%, N 10.98% O 12.35%. MS, M$^+$: 254 (5%), 225 (9%), 197 (22%), 76 (42%), 57 (100%). ^{1}H-NMR (CDCl$_3$) δ 1.3 (t, 3H), 2.4 (q, 2H), 7.47 (d, 2H), 7.39 (d, 2H), 7.35 (d, 2H), 7.27 (s, 3H).

4-(Phenyldiazenyl)phenylhaptanoate [6b]. The procedure is described above, and the yield was 62%, IR (KBr) 1751 cm^{-1} (C=O), 1576 cm^{-1} (Aromatic C=C), 1586 cm^{-1} (N=N). Anal. calcd. for $C_{19}H_{22}N_2O_2$: C 73.52%, H 7.14%, N 9.0%, O 10.31%. Found: C 73.49%, H 7.12%, N 8.92%, O 10.18%. MS, M$^+$: 310 (7%), 225 (9%), 197 (22%), 76 (42%), 57 (100%). ^{1}H-NMR (CDCl$_3$) δ 0.9 (t, 3H),1.4 (s, 8H), 2.4 (d, 2H), 7.47 (d, 2H), 7.38 (d, 2H), 7.36 (d, 2H), 7.28 (s, 3H).

4-(Phenyldiazenyl)phenyldodecanoate [6c]. The procedure is described above, and the yield was 68%, IR (KBr) 1723 cm^{-1} (C=O), 1570 cm^{-1} (Aromatic C=C), 1592 cm^{-1} (N=N). Anal. calcd. for $C_{24}H_{32}N_2O_2$: C 75.75%, H 8.40%, N 7.36%, O 8.41% Found: C 75.49%, H 7.18%, N 6.92%, O 8.28%. MS, M$^+$: 380 (16%), 239 (35%), 225 (100%), 104 (11%), 85 (2%).^{1}H-NMR (CDCl$_3$) δ 0.9 (t, 3H), 1.4 (s, 18H), 2.3 (d, 2H) 7.48 (d, 2 H), 7.37 (d, 2H), 7.33 (d, 2H), 7.28 (s, 3H).

4-(Phenyldiazenyl)phenylhexadecanoate [6d]. The procedure is described above, and the yield was 72%, IR (KBr) 1736 cm^{-1} (C=O), 1578 cm^{-1} (Aromatic C=C), 1605 cm^{-1} (N=N). Anal. calcd. for $C_{28}H_{40}N_2O_2$: C 77.02%, H 9.23%, N 6.42%, O 7.33%. Found: C 77.0%, H 9.18%, N 6.22%, O 7.20%. MS, M$^+$: 436 (9%), 240 (40%), 197 (16%), 105 (41%), 77 (100%), 65 (42%). ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 3H), 1.3 (s, 26H), 2.4 (d, 2H) 7.49 (d, 2H), 7.39 (d, 2H), 7.36 (d, 2H), 7.28 (s, 3H).

4-(Phenyldiazenyl)phenyloctadecanoate [6e]. The procedure is described above, and the yield was 70%, IR (KBr) 1748 cm^{-1} (C=O), 1580 cm^{-1} (Aromatic C=C), 1595 cm^{-1} (N=N), Anal. calcd. for $C_{30}H_{44}N_2O_2$: C 77.54%, H 9.54%, N 6.03%,O 6.89%. Found: C 77.32%, H 9.33%, N 5.88%, O 6.70%. MS, M$^+$: 464 (2%), 239 (60%), 225 (20%), 77 (100%). ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 3H), 1.3 (s, 30H), 2.4 (d, 2H), 7.49 (d, 2H), 7.39 (d, 2H), 7.36 (d, 2H), 7.28 (s, 3H).

Nitro Substituted Phenol Based Azo Mesogens

4-[(2-Nitrophenyl)diazenyl]phenylpropanoate [7a]. The procedure is described above, and the yield was 68%, IR (KBr) 1723 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. for $C_{15}H_{13}N_3O_3$: C 60.20%, H 4.38%, N 14.04%, O 21.38%. Found: C 60.11%, H 4.35%, N 13.98%, O, 21.15%. MS M^+: 299 (3%), 270 (100%), 242 (4%) 150 (7%) 122 (10%). ^{1}H NMR ($CDCl_3$) δ 1.3 (t, 3H), 2.3 (q, 2H), 7.47 (d, 2H), 7.39 (d, 2H), 8.30 (d, 2H), 7.60–7.70 (d, 2H).

4-[(2-Nitrophenyl)diazenyl]phenylhaptanoate [7b]. The procedure is described above, and the yield was 71%, IR (KBr) 1739 cm^{-1} (C=O), 1588 cm^{-1} (Aromatic C=C), 1590 cm^{-1} (N=N). Anal. calcd. for $C_{19}H_{21}N_3O_4$: C 64.21%, H, 5.96%, N 11.82%, O 18.01%. Found: C 64.18%, H 5.91%, N 11.78%, O 17.99%. MS M^+: 355 (8%), 285 (100%), 270 (36%), 150 (4%), 122 (3%). ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 8H), 2.4 (d, 2H), 7.47 (d, 2H), 7.38 (d, 2H), 8.30 (d, 2H), 7.62–7.70 (d, 2H).

4-[(2-Nitrophenyl)diazenyl]]phenyldodecanoate [7c]. The procedure is described above, and the yield was 64%, IR (KBr) 1723 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. for $C_{24}H_{31}N_3O_4$: C 67.74%, H 7.34%, N 9.88%, O 15.04%. Found: C 67.70%, H 7.31%, N 9.85%, O 14.99%. MS M^+: 425 (14%), 284 (20%), 285 (33%), 270 (18%),150 (15%), 122 (100), ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 18H), 2.4 (d, 2H), 7.47 (d, 2H), 7.38 (d, 2H), 8.30 (d, 2H), 7.62–7.70 (d, 2H).

4-[(2-Nitrophenyl)diazenyl]]phenylhexadecanoate [7d]. The procedure is described above, and the yield was 60%, IR (KBr) 1733 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N), Anal. calcd. for $C_{28}H_{39}N_3O_4$: C 69.83%, H 8.16%, N 8.72%, O 13.29%. Found: C 69.81%, H 8.11%, N 8.69%, O 1327%. MS M^+: 481 (21%), 284 (8%), 285 (100%). ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H),1.4 (s, 26H), 2.3 (d, 2H) 7.47 (d, 2H), 7.37 (d, 2H), 8.32 (d, 2H), 7.63–7.70 (d, 2H).

4-[(2-Nitrophenyl)diazenyl]]phenyloctadecanoate [7e]. The procedure is described above, and the yield was 75%, IR (KBr) 1735 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. for $C_{30}H_{43}N_3O_4$: C 70.70%, H 8.50%, N 8.24%, O 12.56%, Found: C 70.68%, H 8.44%, N 8.18%, O 12.51%, MS M^+: 509 (2%), 270 (9%), 242 (5%), 285 (100%) 239 (13%). ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 30H), 2.4 (d, 2H) 7.48 (d, 2H), 7.39 (d, 2H), 8.30 (d, 2H), 7.62–7.70 (d, 2H).

Floro Substituted Phenol Based Azo Mesogens

4-[(2-Florophenyl)diazenyl]phenylpropanoate [8a]. The procedure is described above, and the yield was 77%, IR (KBr) 1723 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. for $C_{15}H_{13}N_2O_3F$: C 66.17%, H 4.81%, N 10.29%, O, 11.75%, F 6.98%. Found: C 66.0%, H 4.71%, N 10.23%, O 11.71%, F 6.92%. MS M^+: 272 (11%), 244 (9%), 123 (32%), 95 (20%), 57 (100%). ^{1}H-NMR ($CDCl_3$) δ 1.4 (t, 3H), 2.4 (q, 2H), 7.48 (d, 2H), 7.39 (d, 2H), 8.15 (d, 2H), 7.40 (d, 1H) 7.28 (d, 1H).

4-[(2-Florophenyl)diazenyl]phenylhaptanoate [8b]. The procedure is described above, and yield was 67%, IR (KBr) 1729 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. for $C_{19}H_{21}N_2O_2F$: C 69.49%, H 6.45%, N 8.53%, O

9.74%, F 5.79%. Found: C 69.42%, H 6.41%, N 8.48%, O 9.68%, F 5.72%. MS M^+: 328 (2%), 272 (5%), 258 (100%), 123 (17%), 95 (4%), 76 (24%) ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 8H) 2.4 (q, 2H), 7.48 (d, 2H), 7.39 (d, 2H), 8.12 (d, 2H), 7.40 (d 1H), 7.28 (d, 1H).

4-[(2-Florophenyl)diazenyl]phenyldodecanoate [8c]. The procedure is described above, and the yield was 62%, IR (KBr) 1743 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. for $C_{19}H_{21}N_2O_2F$: C 69.49%, H 6.45%, N 8.53%, O 9.74%, F 5.79%. Found: C 69.42%, H 6.41%, N 8.48%, O 9.68%, F 5.72%. MS M^+: 398 (100%), 258 (33%), 196 (16%), 155 (5%), 95 (30%), 65 (22%). ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 18H), 2.4 (q, 2H), 7.48 (d, 2H), 7.39 (d, 2H), 8.12 (d, 2H), 7.39 (d, 1H), 7.29 (d, 1H).

4-[(2-Florophenyl)diazenyl)phenylhexadecanoate [8d]. The procedure is described above, and yield was 64%, IR (KBr) 1723 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. for $C_{24}H_{31}N_2O_2F$: C 72.27%, H 7.79%, N 7.03%, O 8.03%, F 4.77%. Found: C 72.27%, H 7.79%, N 6.99%, O 7.98%, F 4.72%. MS M^+: 454 (13%), 258 (23%), 123 (36%), 95 (20%), 76 (100%). ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 26H), 2.4 (q, 2H), 7.48 (d, 2H), 7.39 (d, 2H), 8.12 (d, 2H), 7.39 (d 1H) 7.29 (d, 1H).

4-[(2-Florophenyl)diazenyl)phenyloctadecanoate [8e]. The procedure is described above, and the yield was 71%, IR (KBr) 1736 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. $C_{30}H_{43}N_2O_2F$: C 74.65%, H 8.98%, N 5.80%, O 6.63%, F 3.94%. Found: C 74.58%, H 8.90%, N 5.71%, O 6.54%, F 3.72%. MS M^+: 482 (2%), 258 (39%), 243 (100%), 215 (35%), 123 (14%), 95 (9%). ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 30H), 2.4 (q, 2H), 7.48 (d, 2H), 7.39 (d, 2H), 8.12 (d, 2H), 7.39 (d 1H), 7.28 (d, 1H).

Methoxy Substituted Phenol Based Azo Mesogens

4-[(4-Methoxyphenyl)diazenyl]phenylpropanoate [9a]. The procedure is described above, and yield was 61%, IR (KBr) 1723 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. $C_{16}H_{16}N_2O_3$: C 67.51%, H 5.67%, N 9.85%, O 16.88%, Found: C 67.51%, H 5.60%, N 9.71%, O 16.74%. MS M^+: 284 (6%), 255 (46%), 227 (25%), 211 (31%), 107 (100%), 76 (52%). ^{1}H-NMR ($CDCl_3$) δ 1.3 (t, 3H), 2.4 (q, 2H), 3.8 (s, 3H), 7.48 (d, 2H), 7.39 (d, 2H), 7.33 (d, 2H), 7.20 (d, 2H).

4-[(4-Methoxyphenyl)diazenyl] phenylhaptanoate [9b]. The procedure is as described above. The yield was 74%, IR (KBr) 1723 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. $C_{20}H_{24}N_2O_3$, C 70.56%, H 7.11%, N 8.23%, O 14.10%. Found: C 70.41%, H 7.04%, N 8.11%, O 14.02%. MS M^+: 284 (6%), 255 (46%), 227 (25%), 211 (31%), 107 (100%), 76 (52%). ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 8H), 2.3 (q, 2H), 3.8 (s, 3H), 7.48 (d, 2H), 7.39 (d, 2H), 7.33 (d, 2H), 7.20 (d, 2H).

4-[(4-Methoxyphenyl)diazenyl] phenyldodecanoate [9c]. The procedure is described above, and the yield was 67%, IR (KBr) 1723 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. $C_{25}H_{34}N_2O_3$: C 74.64%, H 8.35%, N 6.82%, O 11.69%. Found: C 74.51%, H 8.30%, N 6.76%, O 11.61%. MS M^+: 410 (4%), 270

(40%), 255 (33%), 107 (20%), 76 (100%). ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 18H), 2.3 (q, 2H), 3.6 (s, 3H), 7.48 (d, 2H), 7.39 (d, 2H), 7.33 (d, 2H), 7.20 (d, 2H).

4-[(4-Methoxyphenyl)diazenyl]phenylhexadecanoate [9d]. The procedure is described above, and the yield was 76%, IR (KBr) 1723 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. $C_{29}H_{42}N_2O_3$: C 74.67%, H 9.07%, N 6.00%, O 10.29%. Found: C 74.64%, H 8.90%, N 5.76%, O 10.21%. MS M$^+$: 466 (6%), 270 (100), 255 (23%), 227 (14%), 107 (16%), 76 (40%). ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 26H), 2.3 (q, 2H), 3.6 (s, 3H) 7.48 (d, 2H), 7.39 (d, 2H), 7.33 (d, 2H), 7.20 (d, 2H).

4-[(4-Methoxyphenyl)diazenyl]phenyloctadecanoate [9e]. The procedure is described above, and the yield was 68%, IR (KBr) 1723 cm^{-1} (C=O), 1586 cm^{-1} (Aromatic C=C), 1596 cm^{-1} (N=N). Anal. calcd. $C_{31}H_{46}N_2O_3$, C 75.26%, H 9.37%, N 5.66%, O 9.70%, Found: C 75.14%, H 9.10%, N 5.36%, O 9.41%. MS M$^+$: 494 (2%), 270 (29%), 255 (100%), 227 (7%), 107 (9%) 76 (21%), 57 (11%). ^{1}H-NMR ($CDCl_3$) δ 0.9 (t, 3H), 1.4 (s, 30H), 2.3 (q, 2H), 3.6 (s, 3H), 7.48 (d, 2H), 7.39 (d, 2H), 7.33 (d, 2H), 7.20 (d, 2H).

Table 1
Transition temperatures and phases

Compound code	n[a]	C	SA	N	I
6a	2	141.5	—	142.20	159.6
6b	6	114.96	—	116.10	132.07
6c	11	88.50	90.60	98.2	109.24
6d	15	71.56	78.40	—	86.06
6e	17	58.50	58.70	—	72.44
7a	2	44.5	—	47.50	52.80
7b	6	48.5	—	49.30	57.20
7c	11	43.40	—	47.10	54.50
7d	15	58.60	61.40	—	72.70
7e	17	73.50	75.40	—	77.50
8a	2	84.70	—	85.20	96.20
8b	6	74.60	—	77.10	85.80
8c	11	58.30	—	62.60	75.40
8d	15	71.70	73.60	78.1	88.44
8e	17	91.20	96.30	99.7	102.50
9a	2	103.60	—	104.40	119.25
9b	6	89.40	—	92.50	102.58
9c	11	69.98	72.20	—	92.20
9d	15	59.40	60.10	—	81.44
9e	17	63.69	78.50	—	88.82

C = Melting temperature fully ordered crystalline temperature.
SA = Smectic A phase, N = Nematic phase, I = Isotropic liquid.
[a]n = No. of carbon atoms in the side chain.

Results and Discussion

All new compounds were characterized by UV, IR, elemental analysis, mass spectra, and ^{1}H-NMR techniques. The absorption band at 216 nm due to –OH group in aromatic esters [1–5] was absent, which gives a clue that –OH group has been esterified. The further confirmation for esterification was obtained by their IR spectra, where peaks due to OH group at 3450–3600 cm^{-1} are absent and a new pea, which is characteristic of esters at 1742–1751cm^{-1}, has appeared. The transition temperatures for four series are recorded in Table 1.

Table 1 shows that mesogens (**6a–e**), having shorter chain lengths, preferably exhibit nematic phase (which is a more disordered phase), while longer chain lengths show a smectic phase (more ordered and pact form).This is true in principle regarding the structure and property relationship accordingly (31). The smectic phases are lamellar in structure, and requires lateral intermolecular forces for their generation. Thus, they are favored by symmetrical molecular structure and longer side alkyl chains, which have van der Waal's forces. In addition, it is believed that longer alkyl chains tend to reduce melting points and allow liquid crystal phases to be exhibited (31). Therefore, as the length of terminal chain increases, the tendency to have a smectic phase also increases and eventually eliminates the nematic phase while transition temperatures also decrease. The mesogens **7a–e** show gradual increase in transition temperatures, as

Table 2

Theoretic calculated polarizability values[a]

Compound code	Molecular formula	Polarizability ±0.5
6a	$C_{15}H_{14}N_2O_2$	29.62
6b	$C_{19}H_{22}N_2O_2$	36.93
6c	$C_{24}H_{32}N_2O_2$	46.07
6d	$C_{28}H_{40}N_2O_2$	53.38
6e	$C_{30}H_{44}N_2O_2$	57.03
7a	$C_{15}H_{13}N_3O_4$	31.87
7b	$C_{19}H_{21}N_3O_4$	39.18
7c	$C_{24}H_{31}N_3O_4$	48.31
7d	$C_{28}H_{39}N_3O_4$	55.62
7e	$C_{30}H_{43}N_3O_4$	59.28
8a	$C_{15}H_{13}N_2O_3F$	29.57
8b	$C_{19}H_{21}FN_2O_2$	36.88
8c	$C_{24}H_{31}FN_2O_2$	46.02
8d	$C_{28}H_{39}FN_2O_2$	53.33
8e	$C_{30}H_{43}FN_2O_2$	56.98
9a	$C_{16}H_{16}N_2O_3$	31.93
9b	$C_{20}H_{24}N_2O_3$	39.29
9c	$C_{25}H_{34}N_2O_3$	48.37
9d	$C_{29}H_{42}N_2O_3$	55.68
9e	$C_{31}H_{46}N_2O_3$	59.34

[a] The ACDLABS software was used for calculating polarizability values of mesogens.

depicted in the above Table 1. This is probably due to a nitro group at lateral position, which facilitates the intermolecular forces and the long chains become attracted and intertwined, and this helps the lamellar packing required for smectic phase generation as reported in the literature (31). Therefore, it is assumed that, Nitro mesogen with a longer side chain (**7c,7d,** and **7e**) shows smectic phases, although the stability is quite reduced as compared to unsubstituted corresponding mesogens (**6c**, **6d,** and **6e**).

Similarly, in **8a–e**, the same trend is observed, but here the stability of nematic and smectic phases is much higher than **7a–e**, showing that a floro substituent at lateral position has a lesser effect as compared to a nitro substituent. This is probably due to a smaller size floro [1.47Å] substituent. The high polarity and sterric effects enable some significant tailoring of physical properties without too much disruption to the liquid crystal phase stability. There are several reports in the literature (32–34), which prove the lateral substituents effect on the thermal stabilities of the compounds. In series **9a–e**, the methoxy group at para position also has less effect on the liquid crystal stability.

In order to enhance the polarizability anisotropy (35) of the molecular core of mesogens, floro, and nitro groups were introduced to enhance polarizability. Table 2 depicts the theoretical calculated values of polarizability (36), which shows that nitro and methoxy groups are powerful polarizable substituents.

Table 3 illustrates the DSC data of some mesogens (**6a–e**, **7a–b**, **8a, b,** and **9a, b**). The magnitude of enthalpy change is proportional to the change in the structural ordering of the phases involved. Typically, a melting transition from a crystalline solid to a liquid crystal phases or the isotropic liquid phase generates a considerably higher enthalpy change of around 102–112 J g^{-1}, which indicates a much higher structural changes (30). However, a liquid crystals to isotropic liquid transition is characterized by a very small enthalpy change (32). Enthalpy and entropy values of the nematic phase transitions shown above in Table 3 agree well with the literature values, which has helped in further confirmation of a mesophase type (31). For instance, the **6a**

Table 3

DSC data of some mesogens (**6a–e**, **7a–b**, **8a, b** and **9a, b**)

Compound code	Transition	$\Delta H/J\,g^{-1}$	$\Delta S/J\,g^{-1}$
6a	Cr-N	45.64	0.127
	N-I	00.26	0.0007
6b	Cr-N	45.25	0.124
	N-I	00.27	0.0007
6c	N-I	00.33	0.0009
7a	Cr-N	46.33	0.135
	N-I	00.29	0.0006
7b	Cr-N	43.11	0.114
	N-I	00.52	0.0014
8a	Cr-N	45.89	0.128
	N-I	00.39	0.0011
8b	Cr-N	45.23	0.125
9a	Cr-N	44.93	0.118
9b	Cr-N	46.20	0.134

Cr = Crystalline, N=Nematic phase, and I = Isotropic liquid.

crystalline to nematic phase involves $\Delta H = 45.64\ J\,g^{-1}$, and $\Delta S = 0.127\ J\,g^{-1}$, which defines the liquid crystal phase.

Conclusions

A series of new mesogens was investigated as possible potential liquid crystal substances, including the effect of side chain and substituents at lateral and para positions on the stability of liquid crystal phases. The study reveals that among the lateral substituents, the nitro group adversely affects the mesophase thermal stabilities more than the floro group. Furthermore, it was observed that transition temperatures of mesogens decrease as the length of side chain increases. However, the shorter aliphatic chains stabilize the nematic phase, whereas, the longer chains stabilize the smectic phase.

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