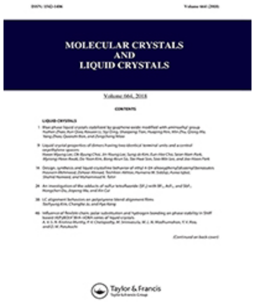


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Design, synthesis and liquid crystalline behavior of ethyl 4-((4-alkoxyphenyl)diazenyl)benzoates

Hasnain Mehmood, Zahoor Ahmad, Tashfeen Akhtar, Humaira M. Siddiqi, Asma Iqbal, Shahid Hameed & Muhammad N. Tahir

To cite this article: Hasnain Mehmood, Zahoor Ahmad, Tashfeen Akhtar, Humaira M. Siddiqi, Asma Iqbal, Shahid Hameed & Muhammad N. Tahir (2018) Design, synthesis and liquid crystalline behavior of ethyl 4-((4-alkoxyphenyl)diazenyl)benzoates, Molecular Crystals and Liquid Crystals, 664:1, 14-23, DOI: 10.1080/15421406.2018.1442779

To link to this article: https://doi.org/10.1080/15421406.2018.1442779

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2018, VOL. 664, 14–23
https://doi.org/10.1080/15421406.2018.1442779

Design, synthesis and liquid crystalline behavior of ethyl 4-((4-alkoxyphenyl)diazenyl)benzoates

Hasnain Mehmood[a], Zahoor Ahmad[a], Tashfeen Akhtar[a], Humaira M. Siddiqi[b], Asma Iqbal[b], Shahid Hameed[b], and Muhammad N. Tahir[c]

[a]Department of Chemistry, Mirpur University of Science and Technology (MUST), Mirpur, AJK, Pakistan; [b]Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan; [c]Department of Physics, University of Sargodha, Punjab, Pakistan

ABSTRACT

A series of ethyl 4-((4-alkoxyphenyl)diazenyl)benzoate is synthesized and the liquid crystalline behavior studied. Synthesized compounds are characterized by FTIR, ^{1}H-NMR, Mass and single crystal XRD. Differential scanning calorimetry was carried out to study the phase transitions and enthalpy changes. Polarizing optical microscopy revealed the mesogenic properties. These techniques revealed that three compounds (2a, 2b, 2f) exhibit liquid crystalline properties in the range of 80–104°C. POM exhibiting focal conical fan like texture which revealed the presence of smectic phases suggestive of their use in LCD and temperature sensing devices, besides 2c can be used as green emitter in OLEDs.

KEYWORDS

Azophenyl; OLED; POM; semestic phases

Introduction

The discovery of liquid crystal state of matter has had major influence on vast fields of science and technology. Various research groups have exploited the significance of this novel state according to its need in various fields such as display systems [1], optoelectronic displays [2] and structure optimization for minimizing light leakage in liquid crystal displays [3]. The chemists synthesize new liquid crystals and establish their mesomorphic properties. Several liquid crystalline materials containing azo, azoxy [4], azoesters, ethers [5] and olefin [6] have been reported. These moieties keep the core linear, assuring the general structural design of linear thermotropic liquid crystals. Other construction design of linear thermotropic liquid crystals include linearly linked ring system, containing rigidity maintaining moieties, flexible chains, enduring dipoles or polarisable groups [7]. Flexible chains are linked either directly to the rings or through some hetero atoms such as Oxygen, Nitrogen and Sulphur. The hetero atoms induce anisotropy in the molecule [8]. Besides maintaining the rigidity of core, Linking groups are also important to induce versatility of applications. Among these linking groups azo group is studied for its interesting optical applications for example holography, optical switching and optical storage devices [9,10], azo dyes [11] and light controlled alignment of liquid crystals [12]. Photo isomerization of aromatic azo compounds (Ar–N=N–Ar’) is much easier than geometrical isomerization of C=C containing compounds. This unique

---

CONTACT Tashfeen Akhtar tashfeenchem@must.edu.pk; tashfeenchem@gmail.com Department of Chemistry, Mirpur University of Science and Technology (MUST), Mirpur-10250, AJK, Pakistan.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

characteristic of azo compounds presents more opportunities in photonic applications. Photo isomerization explains the photo responsive nature of azo compounds including optical switching [13], photo chemical phase transition in holographic applications [14], photo imaging [15], photo responsive dopants [16] and polarization holography [17]. In general azo based liquid crystals have more advantages over the one with ester, ether or olefinic linkages. Azo compounds are thermally stable so they are strong candidates to study photo induced effects [18]. Lateral or terminal substitutions in azo compounds induce liquid crystallinity at low temperature [19]. Considering all these characteristics, present investigation is planned to synthesize a new homologous series containing azo as linking group in order to understand and establish the relation between liquid crystal and molecular structure by changing flexible part. This study includes synthesis, characterization (IR, UV, ^{1}H-NMR, ^{13}C-NMR, Mass spectrometery, Single Crystal XRD) and investigation of mesomorphism through Differential Scanning Calorimetry (DSC) and Polarizing Optical Microscopy (POM).

Experimental

The following reagents were used as received: ethyl 4-aminobenzoate, hydrochloric acid (Merck), sodium nitrite (Merck), phenol (Riedel-de Haen AG Seelze-Hannover), sodium hydroxide (Merck) and alkyl halides of varying chain length (Bromo butane to bromo octadecane) (Merck). Acetone (Riedel-de Haen), methanol and n-hexane (Riedel-de Haen) were used as solvent.

Ultraviolet absorption spectra were recorded on Shimadzu Ultraviolet-1800 spectrophotometer. IR spectra were recorded on Shimadzu nicolet iS10 FTIR spectrophotometer. ^{1}H-NMR spectra were recorded on Bruker Avance 300 MHz NMR spectrometer. X-ray diffractions were recorded on Bruker Kappa APEX II CCD Diffractometer with a graphite monochromator Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature, the structures were resolved using *SHELXL2014*/7 (Sheldrick, 2014). Mesomorphic properties were determined by optical polarizing microscope. The thrmal transition temperatures were taken from the position of peak maxima. The textures of the mesophases were examined on a Leica DM-2500p polarising microscope fitted with temperature controller and a hot stage. Transition temperatures were determined by differential scanning calorimetry using Mettler Toledo Model DSC 851 e, Switzerland. GCMS spectra were recorded using mass spectrometer Model 6890n, inert mass detector (5870) Agilent Technologies, USA.

Synthesis of ethyl 4-((4-alkoxyphenyl)diazenyl)benzoates (2a-2h)

Ethyl 4-((4-hydroxyphenyl)diazenyl)benzoate (0.001 mol) was dissolved in acetone (20 mL) and added potassium carbonate (3 eq), to this reaction mixture respective alkyl halide (1.0 eq) was added and the reaction mixture was subjected to reflux and the completion of the reaction monitored by TLC. After completion the reaction mixture was poured into cold water and the precipitated solid was filtered, dried and recrystallzied from ethanol water.

Ethyl 4-((4-butyloxyphenyl)diazenyl)benzoate (2a)

$\lambda_{max} = 361$ nm; FTIR (ATR): 2958, 1708, 1597, 1473, 1246 cm^{-1}; **^{1}H-NMR** (300 MHz, acetone-d$_6$, δ ppm): 1.0 (t, 3H, CH_3), 1.4 (t, 3H, CH_3), 1.5 (Sextet, 2H, CH_2), 1.8 (quintet, 2H, CH_2), 4.1 (t, 2H, CH_2), 4.4 (quartet, 2H, CH_2), 7.2 (d, 2H, 2xCH, Ar-H), 7.9- 8.0 (m, 4H, 4xCH, Ar-H) and 8.2 (d, 2H, 2xCH, Ar-H); **^{13}C-NMR** (75 MHz, acetone-d$_6$, δ ppm):165.30, 162.63, 155.19, 146.70, 131.74, 130.40, 125.11, 122.28, 114.92, 67.97, 60.86, 31.06, 18.97, 13.71, 13.23; **EIMS**: m/z 326 (M$^+$), 311, 298, 297, 283, 281, 269, 253, 177, 149, 73.

Ethyl 4-((4-pentyloxyphenyl)diazenyl)benzoate (2b)

λ_{max} = 360 nm; FTIR (ATR): 2939, 1708, 1600, 1469, 1260 cm^{-1}; **^{1}H-NMR** (300 MHz, acetone-d$_6$, δ ppm): 0.9–1.0 (t, 3H, CH_3), 1.4–1.6 (m, 7H, CH_3, 2x CH2), 1.8–1.9 (quintet, 2H, CH_2), 4.1–4.2 (triplet, 2H, CH_2), 4.4 (quartet, 2H, CH_2), 7.1–7.2 (d, 2H, 2xCH, Ar-H),7.9-8.0 (m, 4H, 4xCH, Ar-H) and 8.2 (d, 2H, 2xCH, Ar-H); **^{13}C-NMR** (75 MHz, acetone-d$_6$, δ ppm): 165.30, 162.65, 155.20, 146.70, 131.75, 130.42, 125.11, 122.27, 114.95, 68.25, 60.87, 29.73, 28.19, 22.22, 13.69, 13.42; **EIMS**: m/z 340 (M$^+$), 325, 311, 283, 267, 191, 163, 177, 73.

Ethyl 4-((4-hexyloxyphenyl)diazenyl)benzoate (2c)

λ_{max} = 360 nm; FTIR (ATR): 2939, 1702, 1602, 1471, 1255 cm^{-1}; **^{1}H-NMR** (300 MHz, acetone-d$_6$, δ ppm): 0.9 (t, 3H, CH_3), 1.3–1.6 (m, 9H, CH_3, 3x CH_2), 1.8–1.9 (quintet, 2H, CH_2), 4.1–4.2 (triplet, 2H, CH_2), 4.4 (quartet, 2H, CH_2), 7.1–7.2 (d, 2H, 2xCH, Ar-H),7.9-8.0 (m, 4H, 4xCH, Ar-H) and 8.2 (d, 2H, 2xCH, Ar-H); **^{13}C-NMR** (75 MHz, acetone-d$_6$, δ ppm): 165.30, 162.65, 155.20, 146.69, 131.75, 130.42, 125.12, 122.28, 114.95, 68.27, 60.87, 31.42, 29.74, 25.52, 22.41, 13.70, 13.44; **EIMS**: m/z 354 (M$^+$), 339, 326, 325, 283, 281, 269, 191, 177, 73.

Ethyl 4-((4-heptyloxyphenyl)diazenyl)benzoate (2d)

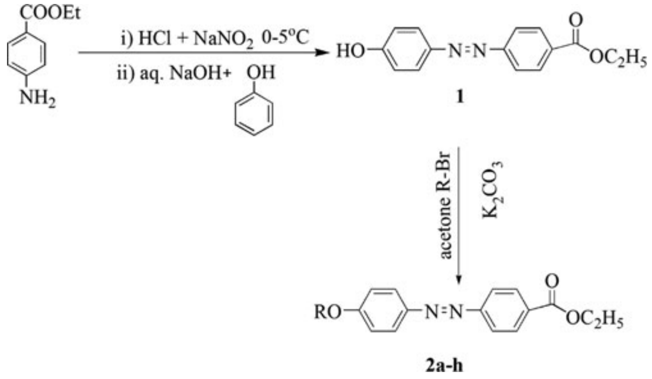
λ_{max} = 360 nm; FTIR (ATR): 2946, 1714, 1602, 1500, 1265 cm^{-1}; **^{1}H-NMR** (300 MHz, acetone-d$_6$, δ ppm): 0.9 (t, 3H, CH_3), 1.3–1.6 (m, 11H, CH_3, 4x CH_2), 1.8–1.9 (quintet, 2H, CH_2), 4.1–4.2 (triplet, 2H, CH_2), 4.4 (quartet, 2H, CH_2), 7.1–7.2 (d, 2H, 2xCH),7.9- 8.0 (m, 4H, 4xCH) and 8.2 (d, 2H, 2xCH); **^{13}C-NMR** (75 MHz, acetone-d$_6$, δ ppm): 165.30, 162.65, 155.20, 146.69, 131.75, 130.42, 125.12, 122.28, 114.95, 68.27, 60.87, 31.67, 29.74, 29.48, 25.79, 22.40, 13.70, 13.48; **EIMS**: m/z 368 (M$^+$), 339, 283, 269, 177, 105, 73.

Ethyl 4-((4-octyloxyphenyl)diazenyl)benzoate (2e)

λ_{max} = 360 nm; FTIR (ATR): 2920, 1712, 1579, 1469, 1260 cm^{-1}. (300 MHz, acetone-d$_6$, δ ppm): 0.9 (t, 3H, CH_3), 1.3–1.6 (m, 13H, CH_3, 5x CH_2), 1.8–1.9 (quintet, 2H, CH_2), 4.1–4.2 (triplet, 2H, CH_2), 4.4 (quartet, 2H, CH_2), 7.1–7.2 (d, 2H, 2xCH),7.9- 8.0 (m, 4H, 4xCH) and 8.2 (d, 2H, 2xCH); **^{13}C-NMR** (75 MHz, acetone-d$_6$, δ ppm):165.30, 162.65, 155.23, 146.73, 131.77, 130.39, 125.09, 122.25, 114.95, 68.28, 60.83, 31.66, 29.70, 29.44, 29.19, 25.82, 22.41, 13.68, 13.45; **EIMS**: m/z 283, 269, 177, 73.

Ethyl 4-((4-decyloxyphenyl)diazenyl)benzoate (2f)

λ_{max} = 361 nm; FTIR (ATR): 2918, 1712, 1600, 1469, 1262 cm^{-1}; **^{1}H-NMR** (300 MHz, acetone-d$_6$, δ ppm): 0.9 (t, 3H, CH_3), 1.2–1.6 (m, 15H, CH_3 6xCH_2), 1.8–1.9 (quintet, 2H, CH_2), 4.1–4.2 (triplet, 2H, CH_2), 4.4 (quartet, 2H, CH_2), 7.1–7.2 (d, 2H, 2xCH, Ar-H), 7.9- 8.0 (m, 4H, 4xCH, Ar-H) and 8.2 (d, 2H, 2xCH, Ar-H); **^{13}C-NMR** (75 MHz, acetone-d$_6$, δ ppm): 165.31, 162.66, 155.23, 131.77, 130.41, 125.10, 114.97, 68.28, 60.86, 31.73, 25.81, 22.43, 13.67, 13.46. **EIMS**: m/z 283, 269, 177, 73.



Scheme 1. Synthesis of ethyl 4-[(4-alkoxyphenyl)diazenyl]benzoate.

Ethyl 4-((4-hexadecyloxyphenyl)diazenyl)benzoate (2g)

λ_{max} = 359 nm; FTIR (ATR): 2916, 1712, 1583, 1463, 1260 cm^{-1}; **^{1}H-NMR** (300 MHz, acetone-d_6, δ ppm): 0.9 (t, 3H, CH_3), 1.2–1.5 (m, 29H, CH_3 13xCH_2), 1.8–1.9 (quintet, 2H, CH_2), 3.5 (triplet, 2H, CH_2), 4.4 (quartet, 2H, CH_2), 7.1–7.2 (d, 2H, 2xCH, Ar-H), 8.0 (m, 4H, 4xCH, Ar-H) and 8.2 (d, 2H, 2xCH, Ar-H); **^{13}C-NMR** (75 MHz, DMSO-d_6, δ ppm): 165.34, 162.75, 131.91, 130.43, 125.12, 122.28, 115.00, 68.39, 60.88, 33.98, 32.74, 31.75, 29.78, 29.52, 28.76, 28.50 28.24 27.91 25.81, 22.44, 13.74, 13.50; **EIMS**: m/z 283, 269, 177, 73.

Ethyl 4-((4-octadecyloxyphenyl)diazenyl)benzoate (2h)

λ_{max} = 358 nm; FTIR (ATR): 2916, 1712, 1585, 1463, 1282 cm^{-1}; **^{1}H-NMR** (300 MHz, acetone-d_6, δ ppm): 0.9 (t, 3H, CH_3), 1.2–1.6 (m, 33H, CH_3 15xCH_2), 1.8–1.9 (quintet, 2H, CH_2), 3.5 (triplet, 2H, CH_2), 4.4 (quartet, 2H, CH_2), 7.1–7.2 (d, 2H, 2xCH, Ar-H), 8.0 (m, 4H, 4xCH, Ar-H) and 8.2 (d, 2H, 2xCH, Ar-H); **^{13}C-NMR** (75 MHz, DMSO-d_6, δ ppm): 171.36, 169.85, 169.22, 167.40, 166.68, 130.43, 125.12, 122.27, 115.01, 68.28, 60.83, 34.01, 32.71, 31.72, 29.76, 29.25, 27.88, 25.77, 22.42, 13.47; **EIMS**: m/z 345, 283, 269, 177, 73.

Results and discussion

The synthesis of the target molecules (**2a-h**) was achieved by the diazo coupling of ethyl 4-aminobenzoate and phenol, followed by the condensation with alkyl halides of varying chain length under basic conditions (Scheme 1).

Where R = C_nH_{2n+1} and n = 4, 5, 6, 7, 8, 10, 16 and 18.

The physical data of the series of compounds in presented in Table 1. The synthesis was initially studied using FTIR spectra, where the broad absorption of the OH disappeared in going from the reactant to product. This disappearance of broad OH absorption and appearance of aliphatic CH stretching below 3000 cm^{-1} was strong indication of the formation of desired ether linkage.

The synthesized compounds were also characterized by NMR spectroscopy. In ^{1}HNMR spectrum signals in range 1.0–1.5 ppm were assigned to alkyl chain and a down field triplet signals at 4.1–4.5 ppm indicated the alkyloxy linkage. The signals of the aromatic protons exhibited no significant shift from the parent intermediate ethyl 4-(4-hydroxyphenyldiazenyl) benzoate. The synthesis was varified by the 13C-NMR as well and besides teh signals of aromatic carbons new signals in the alipahtic region corresponding to variable alkyl chaing were

Table 1. Physical data of the Ethyl 4-[(4-alkoxyphenyl)diazenyl]benzoate.

Sr. no	Appearance	R_f value*	Yield %	Melting point
2a	Orange red solid	0.70	67%	80–98°C
2b	Orange red solid	0.73	64%	81–92°C
2c	Orange red solid	0.73	76%	80–96°C
2d	Orange red solid	0.75	63%	79–96°C
2e	Orange solid	0.75	72%	82–98°C
2f	Orange solid	0.75	72%	101–112°C
2g	Orange solid	0.79	74%	58–75°C
2h	Orange solid	0.86	70%	68–88°C

*(n-hexane: Acetone 3:1)

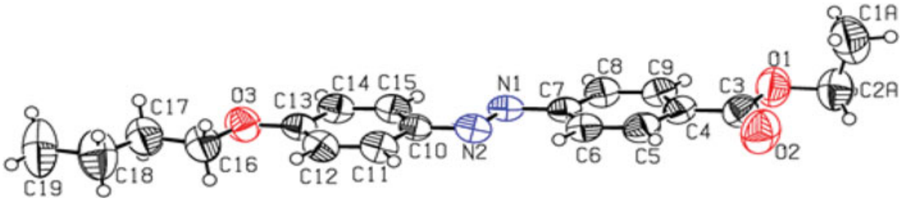


Figure 1. Structure of ethyl 4-((4-butyloxyphenyl)diazenyl)benzoate (2a) in crystal, thermal ellipsoid drawn at 50% probability level.

observed. The important signals are the appearance of two alkoxy carbon at around 60 and 68 ppm, respectivley for the ester and ethre linkages. Although the middle carbons of the chaign exhibitting less number of signals as compared to the total number of carbons and this is because of the overlappign of the signals due to negligible effect of the electronegative group as the distance increases. However, the signals of two methyl groups one for the CH of the ester and the other for the terminal CH_3 of the alkyl chaing were found at the most upfield of the spectrum, which confirmed the formation of proposed ether linkage. The synthesis was further confirmed by the mass spectromety using EI-MS. The presence of molecular ion and the fragments at different mass to charge ratio corresponidng to characteristic parts of the structure confirmed the desired synthesis. The mass fragmentation pattern exhibiting the α-cleavage of ester leading to loss of 73 amu and exhibitin a fragment at m/z 196+R. the mass spectra also exhibit the fragment of alkoxyphenyl at m/z 92+R and a fragment at M − 92 +R, this fragments results by the fragmentation from of the azo linkage, other importatn fragments for shorter chain lengths are exhibited in the scheme below (Scheme 2). However with the increase in the chain length it looks from the spectral data that the stability is decreased or there is possible decompositon during the vaporization and ionization and few fragments are seen in the specra.

The single crystal analysis of **2a** and **2b** further supported the proposed structures and synthetic design. The ORTEP diagram of 2a and 2b is shown in the Figs. 1 and 2, respectively.

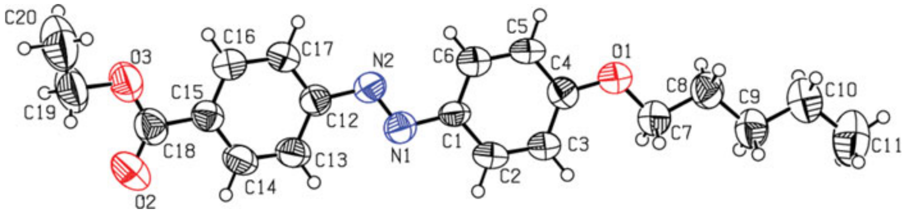
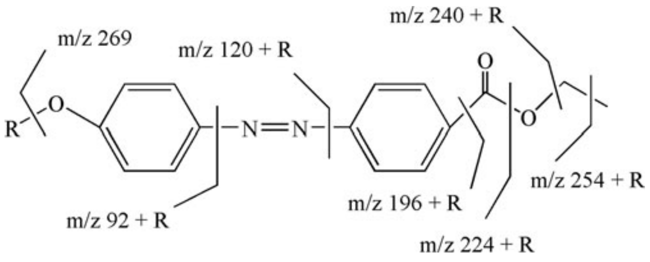


Figure 2. Structure of ethyl 4-((4-pentyloxyphenyl)diazenyl)benzoate (2b) in crystal, thermal ellipsoid drawn at 50% probability level.



Scheme 2. Sugested mass fragmentation pattern of ethyl 4-[(4-alkoxyphenyl)diazenyl]benzoate.

Torsional angle of 180° between N1, N2, C7, C10 and N1, N2, C1, C12 in 2a and 2b, respectively, confirmed that molecule is in its stable *trans* form across the N=N bond. The crystal and refinement data in presented in Table 2 and selected bond lengths and bond angles are shown in Table 3. The crystallographic data can be obtained for the compounds with CCDC 1541387 (**2a**) and CCDC 1541388 (**2b**) from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Mesomorphic properties of all the synthesized compounds were investigated by employing DSC and POM techniques. DSC therms indicating phase transitions corresponding to heating/cooling cycle at the rate of 10°C/min. All synthesized compounds except (**2a**), (**2b**) and (**2f**) displayed sharp melting points indicating non-mesogenic behavior. Figure 2 shows the transition temperatures versus number of carbon atoms in alkyl chain. DSC thermogram of **2a** was recorded by taking three scans two heating and one cooling scan at the rate of 10°C/min. The DSC result revealed the presence of more than one transition for **2a**, **2b** and **2f** which was further studied under POM.

Table 2. Single crystal XRD data of compounds **2a** and **2b**.

	2a	2b
Chemical formula	$C_{19}H_{22}N_2O_3$	$C_{20}H_{24}N_2O_3$
M_r	326.38	340.41
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$
Temperature (K)	296	296
a, b, c (Å)	21.796 (2), 7.4870 (8), 22.740 (2)	15.097 (4), 6.0081 (15), 41.938 (12)
β (°)	101.917 (6)	95.197 (7)
V (Å^3)	3630.9 (7)	3788.4 (18)
Z	8	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.08	0.08
Crystal size (mm)	$0.45 \times 0.26 \times 0.18$	
Data collection		
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27182, 6711, 2251	14672, 3719, 1190
R_{int}	0.065	0.113
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0.606	0.617
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.076, 0.283, 1.00	0.084, 0.213, 0.98
No. of reflections	6711	3719
No. of parameters	438	229
No. of restraints	10	
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$(\Delta/\sigma)_{\max}$	3.228	
$\Delta\rangle_{\max}$, $\Delta\rangle_{\min}$ (e Å^{-3})	0.40, −0.37	0.17, −0.14

Table 3. Selected bond lengths and bond angles of ethyl 4-((4-butyloxyphenyl)diazenyl)benzoate.

	Bond length (Å)			
Bond type	2a	Bond length (Å)	2b	Bond length
CH_3–CH_2–	C1A C2A	1.494	C19 C20	1.494
–CH_2–O–CO	C2A O1	1.469	C19 O3	1.469
COO	C3 O1	1.329	C18 O3	1.329
C=O	C3 O2	1.207	C18 O2	1.207
C-Ar	C3 C4	1.470	C18 C15	1.470
Ar C=C	C4 C9	1.376	C15 C14	1.357
O–C_6H_5	C13 O3	1.359	C4 O1	1.359
–N=N–	N1 N2	1.251	N1 N2	1.251

Table Selected bond angles of **2a** and **2b**.

2a Bonds	Angle (deg)	2b Bonds	Angle (deg)
O1-C2A-C1A	101.0	O3-C19-C20	108.8
O2-C3-O1	120.6	O2-C18-O3	123.3
O1-C3-C4	113.4	O3-C18-C15	112.5
C9-C4-C5	118.8	C14-C15-C16	118.3
O3-C16-C17	107.3	O1 -C7-C8	108.6
C17-C18-C19	112.5	C9-C10-C11	114.9

The heating and cooling scans of **2a** indicated enantiotropic transitions, a small transition at 73°C and the crystallization peak at 87°C. However when **2a** observed under polarizing optical microscope, liquid crystal phase started appearing at 104°C with broken focal conic texture, which on further cooling developed a conical fan like texture at 95°C, characteristic of the smectic C mesophase were observed which are presented in Fig. 3. This mesogenic behavior lasts upto 80°C and disappeared at further cooling and converted to crystal phase.

The compound **2b**, with just an increment of a methylene unit exhibited a single broad endothermic peak at 91°C whereas two exothermic peaks appeared at 83°C and 55°C, respectively, in cooling scan of DSC. When studied under POM, at 94°C clear circular focal conic structures started appearing and this texture was stable up to 60°C showing a range of almost 30°C as compared to the lower homologue. This behavior is attributable to the bent core structure and a pentyloxy chain in **2b** which breaks the symmetry of the layered structures resulting in development of smectic phase (Fig. 4).

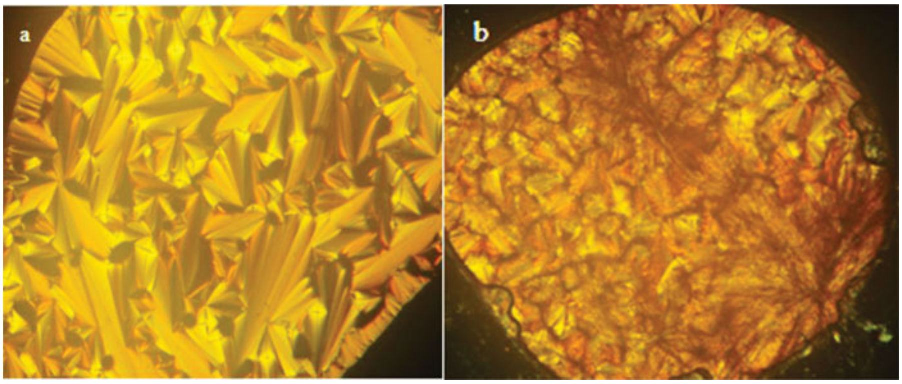


Figure 3. (a) Smectic phase in 2a at 85°C (b) smectic phase in **2f** at 91°C.

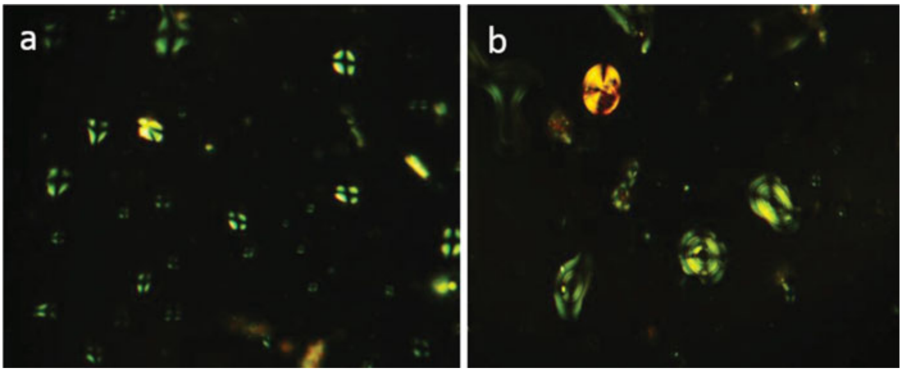


Figure 4. 2b at (a) 89°C and (b) 90°C.

It was thought that by appending different alkoxy chain lengths a regular change in mesogenic properties would be observed but no regular trend in mesogenic properties was observed. The compounds with 6,7,8,9,16 and 18 spacer lengths exhibited only a single large peak corresponding to the melting transition in their DSC thermograms. Whereas the heating and cooling scans of **2f** also showed enantiotropic behavior and two peaks indicating the presence of mesophase were observed. Further investigation under POM revealed clear focal conical fan like texture which appeared at 103°C till 91°C with range of 12°C, further cooling converted to the crystalline phase at 90°C.

The inappropriate magnitude of anisotropic forces of end-to-end intermolecular interactions, inauspicious molecular rigidity and unfavorable flexibility to maintain the parallel orientation of molecules in floating conditions is responsible for the presence of smectic phase. However, favorable molecular rigidity maintained by the −N=N− linking the phenyl rings, *n*-alkoxy group connected to the terminal rings and overall satisfactory molecular polarizability favor the lamellar packing of **2a, 2b** and **2f** in their crystal lattice. Thus, these homologues having suitable magnitudes of intermolecular anisotropic forces preferably maintain layered arrangement in crystal lattices. These layers show sliding layered arrangement of molecules when exposed to definite range of temperature under exposed thermal vibrations. As a result of this thermal exposition the forces which are holding the layers in crystal are weakened than the force of attraction between molecules at mesomorphic transition. Thus, layers slide over each other and result into the formation of smectic mesophase. Further heating leads to the weakening of intermolecular forces to such extent that do not allow the molecules to slide

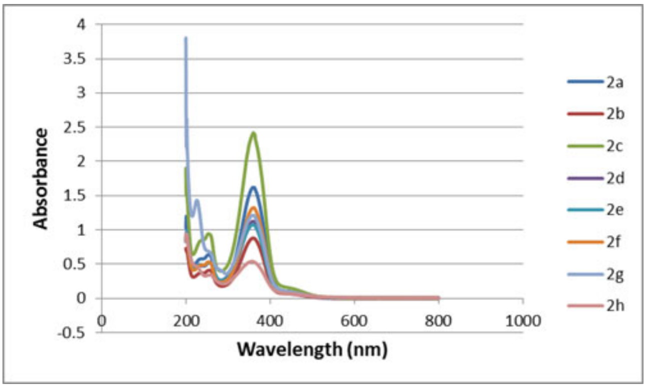


Figure 5. UV-Vis absorption of compounds 2a–2h.

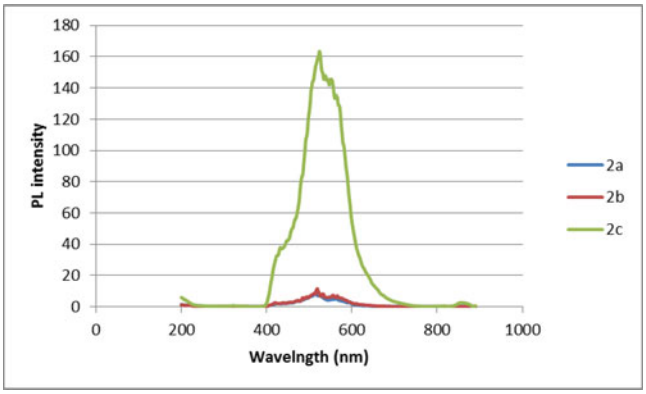


Figure 6. Photoluminescence spectra of butyloxy (**2a**), pentyloxy (**2b**) and hexyloxy (**2c**).

over each other in layers, hence parallel orientation is disrupted and the sample is converted to isotropic liquid. On the other hand, same smectic phases appear when cooled the isotropic liquid. The results established that all the mesogenic members of this synthesized series of compounds displayed almost similar smectic phases with conical fan like textures due to presence of identical azo and ester groups. Whereas by increasing the methylene units in terminal or tail decreased the liquid crystal transition range increasing the melting temperatures.

In order to study the photoluminescent properties UV-Vis and PL spectra were recorded in solution of acetone. The emission spectra were recorded by the excitation wavelength taken from the UV-Vis spectra. Figures 5 and 6 shows UV-Vis absorption and photoluminescence spectra of compounds, respectively. The compounds 2c after excitation at 351 nm exhibit emission at 524 nm hence can be used as green emitter.

Conclusion

Current investigation was designed to contain two phenyl rings bonded through −N=N− to constitute the rigid core. Members of the investigated series are entirely smectogenic phase. Only three members C4, C5 and C10 showed liquid crystalline behavior.

References

[1] Naemura, S. (2001). *Adv. LCD Technol. Displays*, *22*, 1.
[2] Demus, D. (1988). *Mol. Cryst. Liq. Cryst.*, *165*, 45.
[3] Kim, W. S., Elston, S. J., & Raynes, F. P. (2008). *Display*, *29*, 458.
[4] Demus, D. (1989). *Liq. Cryst.*, *5*, 75.
[5] Patel, V. R., & Doshi, A. V. (2010). *Derpharma Chemica*, *2*, 429.
[6] Suthar, D. M., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cry.*, *569*, 64.
[7] Sandhya, D., & Vora, R. A. (2015). *Mol. Cryst. Liq. Cryst.*, *623*, 56.
[8] Kumar, S. (2001). *Experimental Study of Physical Properties and Phase Transitions*, Cambridge: Cambridge University Press.
[9] Ruslim, C., & Ichimura, K. (1999). *J. Mater. Chem.*, *9*, 673.
[10] Thaker, B. T., Kanojiya, J. B., & Tandel, R. S. (2010). *Mol. Cryst. Liq. Cryst.*, *528*, 120.
[11] Lai, L. L., Wang, E., Liu, Y. H., & Wang, Y. (2002). *Liq. Cryst.*, *29*, 871.
[12] Komitov, L., Ichimura, K., & Strigazzi, A. (2000). *Liq. Cryst.*, *27*, 51.
[13] Ikeda, T., & Tsutsumi, O. (1995). *Science*, *268*, 1873.
[14] Yu, Y., & Ikeda, Y. (2004). *J. Photochem. Photobio. C: Photochem. Rev.*, *5*, 247.

[15] Kozlovsky, M. V., Shibaev, V. P., Stakhanov, A. I., Weyrauch, T., & Iaase, W. I. (1998). *Liq. Cryst.*, *24*, 759.

[16] Ruslim, C., & Ichimura, K. (1998). *Chem. Lett.*, *27*, 789.

[17] Anderle, K., & Wendorff, J. (1994). *Mol. Cryst. Liq. Cryst.*, *243*, 51.

[18] Prasad, V. (2001). *Liq. Cryst.*, *28*, 145.

[19] Kaspar, M., Hamplova, V., Pakhomov, S. A., Stibor, I, Sverenya, K. H., Bubnov, A. M., Glogarova, M., & Vanek, P. (1997). *Liq. Cryst.*, *22*, 557.