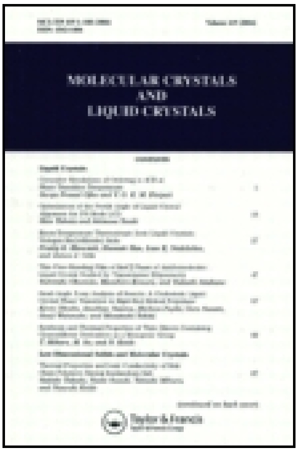

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Studies of Calamitic Liquid Crystalline Compounds Involving Ester-Azo Central Linkages with a Biphenyl Moiety

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Version of record first published: 07 Oct 2011

To cite this article: B. T. Thaker, Y. T. Dhimmar, B. S. Patel, D. B. Solanki, N. B. Patel, N. J. Chothani & J. B. Kanojiya (2011): Studies of Calamitic Liquid Crystalline Compounds Involving Ester-Azo Central Linkages with a Biphenyl Moiety, Molecular Crystals and Liquid Crystals, 548:1, 172-191

To link to this article: http://dx.doi.org/10.1080/15421406.2011.591677

Mol. Cryst. Liq. Cryst., Vol. 548: pp. 172–191, 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.591677

Studies of Calamitic Liquid Crystalline Compounds Involving Ester-Azo Central Linkages with a Biphenyl Moiety

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*Two mesogenic homologous series involving ester-azo central linkages with a biphenyl moiety have been synthesized, such as 4′-[(4-*n*-alkoxyphenyl)diazenyl]biphenyl-4-ol (series I) and 4′-[(4-*n*-alkoxyphenyl) diazenyl]-4-butoxy phenyl biphenyl-4-carboxylate (series II). Azobiphenyl of series I having a free hydroxyl group with strong hydrogen bonding exhibits a high-temperature enantiotropic smectic phase. Whereas in series II, compounds containing C_1–C_8 carbon atoms exhibit only a monotropic smectic phase and compounds with C_{10}, C_{12}, C_{14}, and C_{16} atoms show an enantiotropic smectic phase. These compounds were characterized by elemental analysis, FT-IR, ^{1}H-NMR, and mass spectral studies. The phase transition and mesogenicity of these substances were studied by polarizing optical microscopic and differential scanning calorimetric techniques. Their thermal stabilities and other characteristics are discussed.*

Keywords Biphenyl; ester-azo; nematic and mesophase; smectic

Introduction

While designing new liquid crystal molecules with definite properties, it is necessary to keep in mind that their mesogenic behavior is strongly influenced by the structure of the rigid molecular core and by the lateral substitution on the aromatic rings, with the position of the substituted ring in the molecular core being important [1]. Liquid crystal oligomers consist of molecules containing two or more mesogenic units interconnected via flexible spacers, most commonly alkyl chains [2–5]. There is substantial literature on the studies of biphenyl and its derivatives. 2,3,4-monosubstituted biphenyls have been studied extensively by various workers [6–13] for their molecular geometry, crystallization behavior, crystal packing, and thermal motion, while the literature on growth and structural aspects of linearly chained biphenyls (liquid crystals) is quite insufficient.

Biphenyl esters are typical mesogens with various mesophases having different degrees of order according to substituents [14]. There are many examples of rigid, extended chemical subunits in mesogens. The most common subunit used in synthesizing

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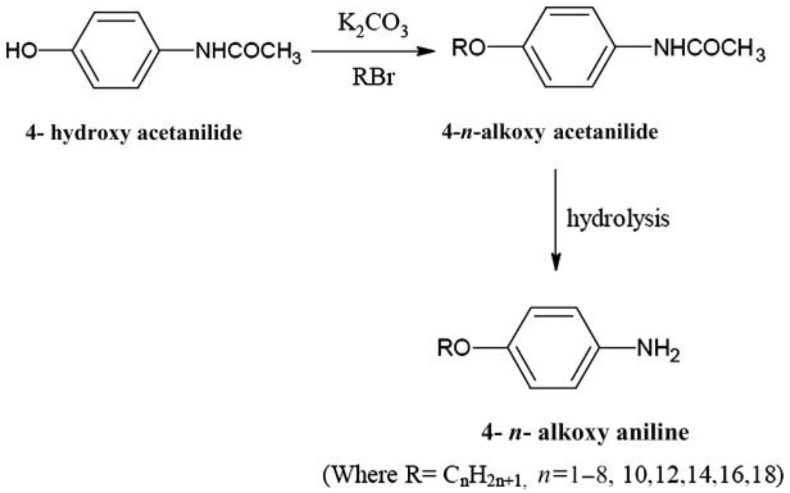
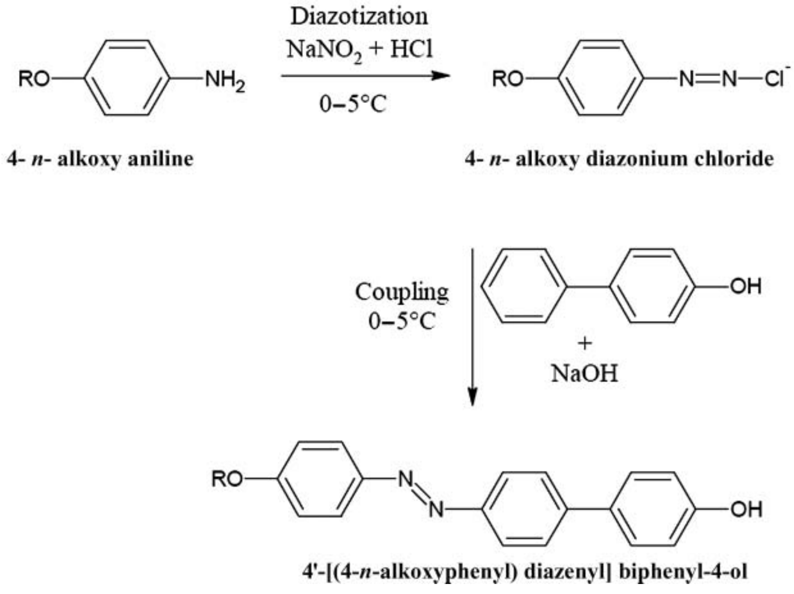
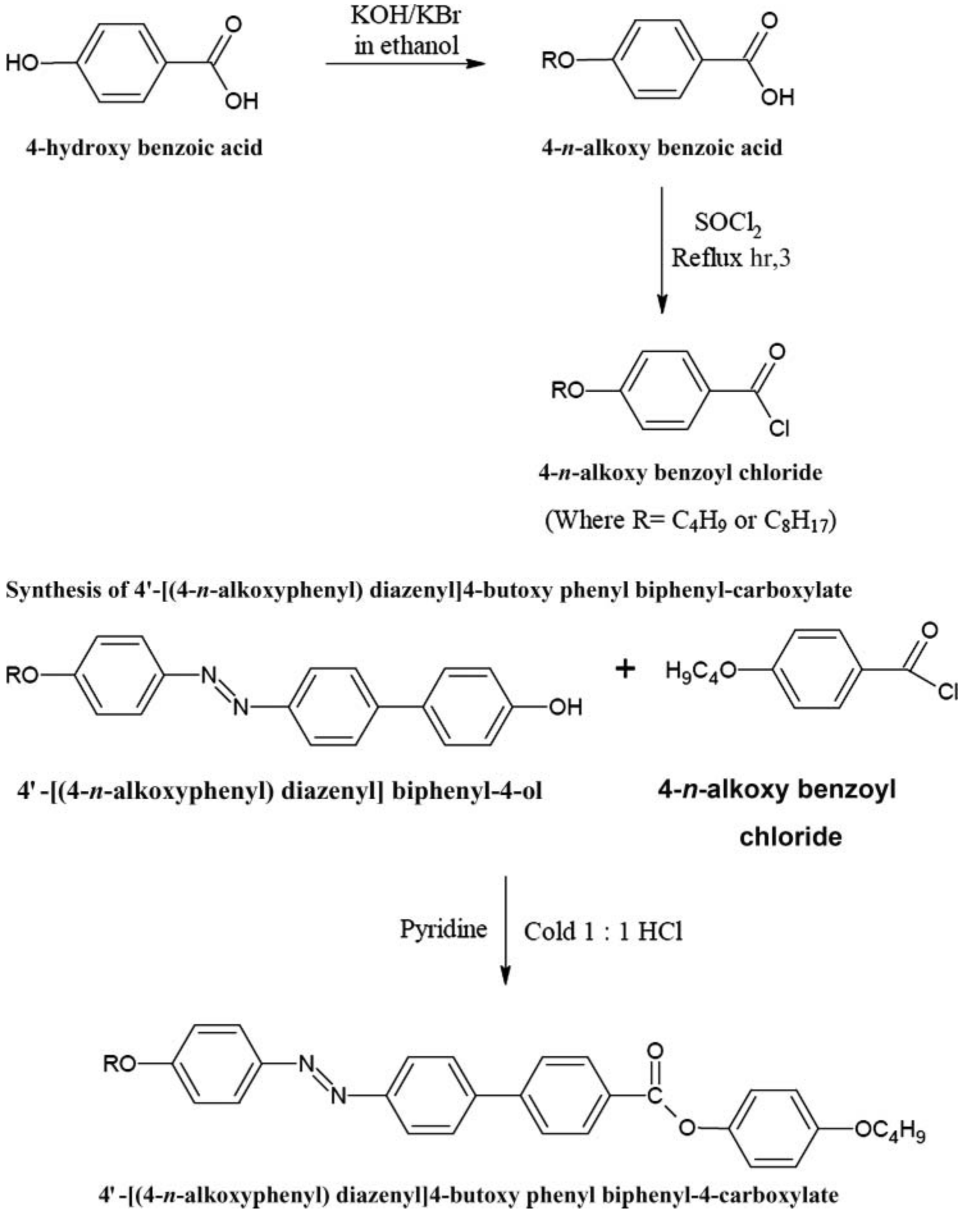


Synthesis of 4'-[(4-*n*-alkoxyphenyl)diazenyl]biphenyl-4-ol



Scheme 1. Series I: synthesis of 4-*n*-alkoxy anilines.

calamitic liquid crystals is the linearly para-substituted phenyl ring [15]. Functionalized azobenzenes were among the first successful nematic liquid crystals used in the display industry [16–20], which constitute an important class of materials for information processing and storage and are being explored as molecular photoswitches. Recently, Michael Hird et al. studied the mesomorphic properties of ortho difluoroterphenyls with a bulky terminal chain [21]. Johnson et al. [22] have synthesized a homologous series of



Scheme 2. Series II: synthesis of 4-*n*-alkoxy benzoyl chlorides.

4-(4-alkylphenylazo)phenols. An attempt has been made to synthesize two series of compounds by using 4-hydroxy biphenyl instead of phenol.

Experimental Methods

Reagents and Techniques

4-hydroxy benzoic acid, alkyl bromide (Lancaster, England), and 4-hydroxy biphenyl were used without further purification. Acetone, ethanol, methanol, hydrochloric acid (HCl),

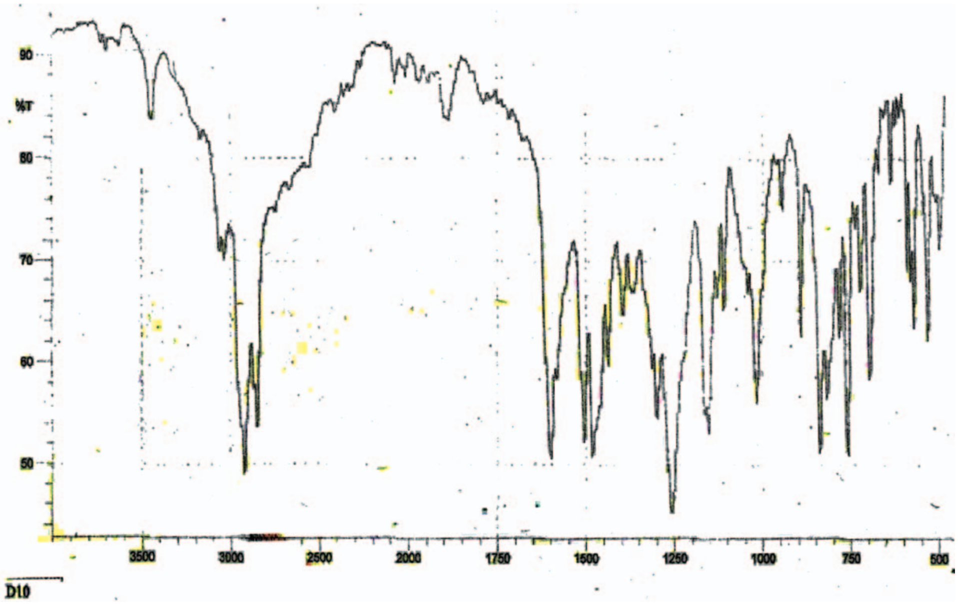


Figure 1. FT-IR spectra of compound A_{10} (series I).

KOH, $NaNO_2$, NaOH, and thionyl chloride were supplied by Polypharm Mumbai, India; certain solvents and reagents were used after distillation and purification by using the standard methods described in the literature [23]. Other auxiliary chemicals were of laboratory grade. Elemental analyses (C, H, N) were performed at the Central Drug Research Institute (CDRI), Lucknow, India. Infrared spectra were recorded by a Perkin-Elmer 2000 FT-IR spectrophotometer in the frequency range 4000–400 cm^{-1} with samples embedded in KBr

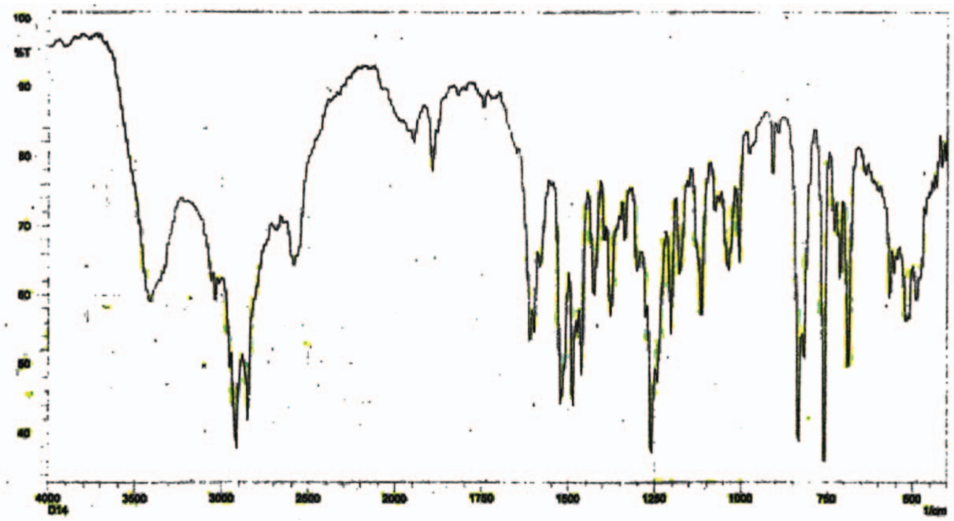


Figure 2. FT-IR spectra of compound A_{14} (series I).

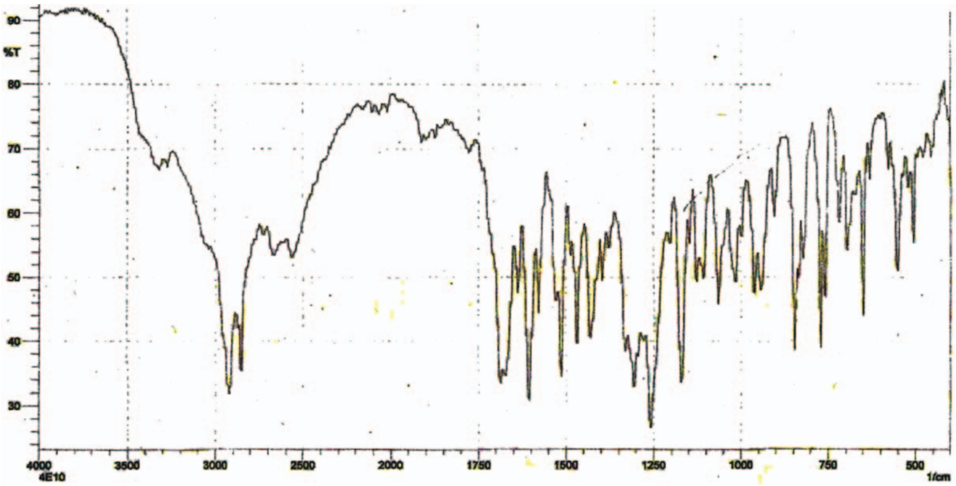


Figure 3. FT-IR spectra of compound B_{10} (series II).

discs. ^{1}H-NMR spectra of the compounds were recorded by a Jeol-GSX-400 instrument using $CDCl_3$ as a solvent and tetramethylsilane as an internal reference at SAIF, Panjab University, Chandigarh, India. Also, mass spectra of the compounds were recorded at SAIF. Thin layer chromatography (TLC) analyses were performed using aluminum-backed silica-gel plates (Merck60 F524) and examined under shortwave UV light. The phase transition temperatures were measured using Shimadzu DSC-50 at heating and cooling rates of 10°C min^{-1}, respectively. The textures of the mesophase were studied using a Leitz Labourlux polarizing microscope provided with a Kofter heating stage at the Applied Chemistry Department, M. S. University of Baroda, Vadodara, Gujarat, India.

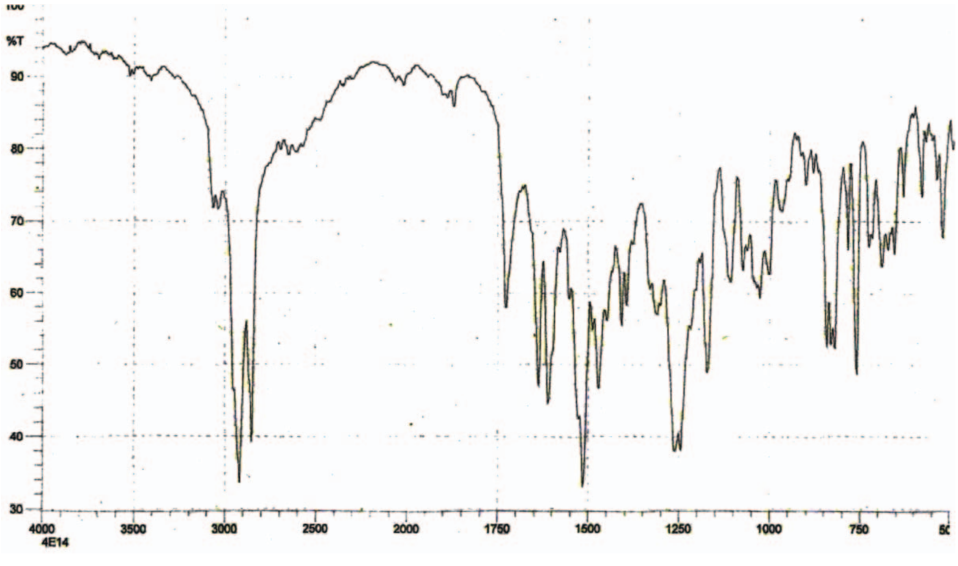


Figure 4. FT-IR spectra of compound B_{14} (series II).

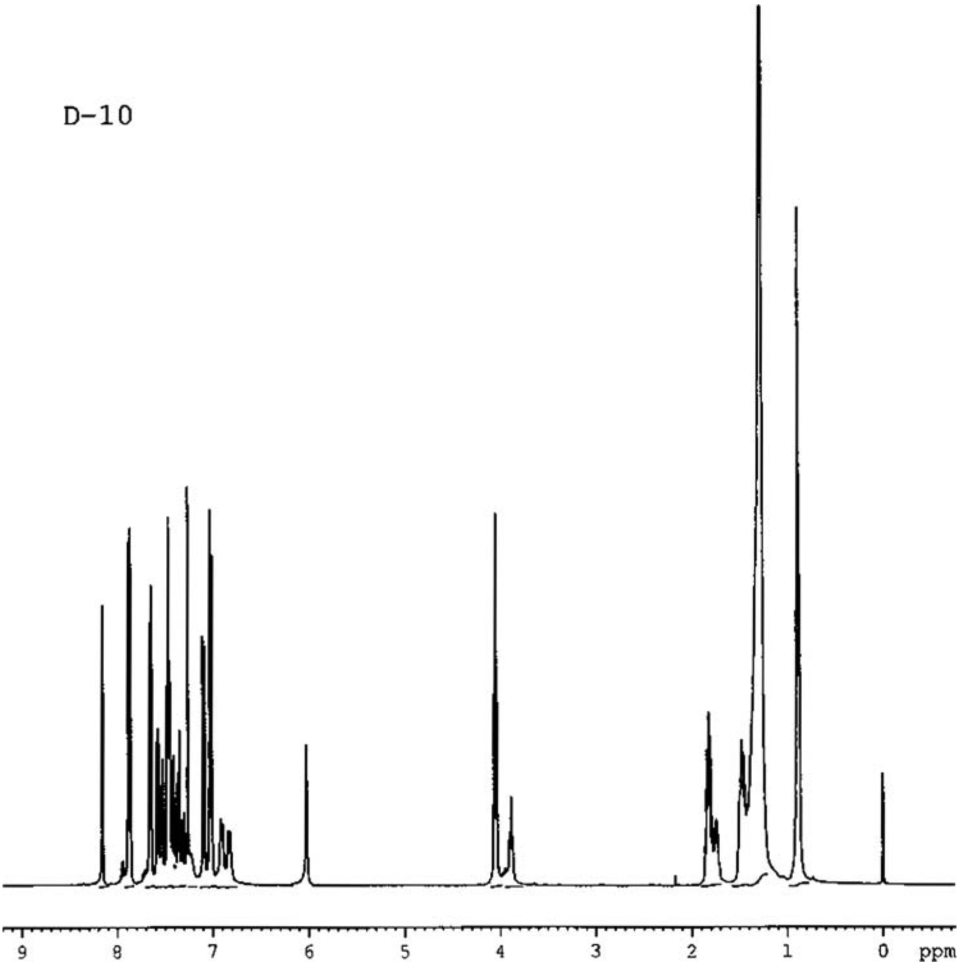
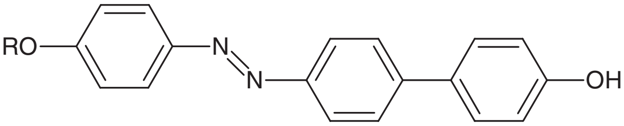


Figure 5. ^{1}H-NMR spectra of compound A_{10} (series I).



4′-[(4-*n*-alkoxyphenyl)diazenyl] biphenyl-4-ol (where $R = C_{10}H_{21}$ series 1)

Synthesis

Series I compounds synthesized as per Scheme 1

*Synthesis of 4-n-Alkoxy Anilines. 4-*n*-Alkoxy Acetanilides*. Paracetamol (0.1 mol), anhydrous potassium carbonate (0.15 mol), respectively, *n*-alkyl bromide (0.15 mol), and dry acetone (60 ml) were taken in a round-bottom flask (RBF) provided with a condenser and a guard tube. The reaction mixture was refluxed in a water bath for 8–10 hr. The whole mass was then added to water and extracted with ether. The ether was evaporated and the residual solids were obtained as alkoxy acetanilides.

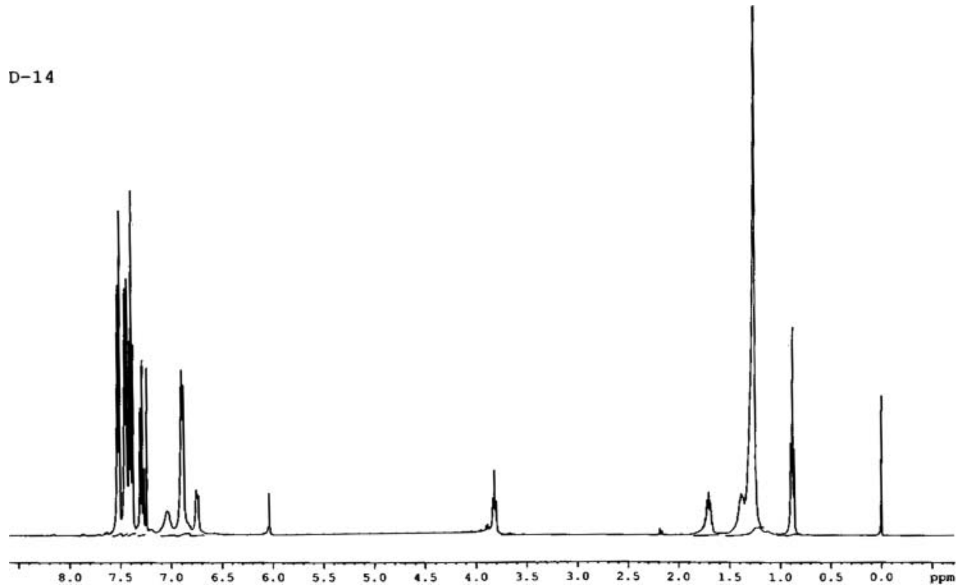
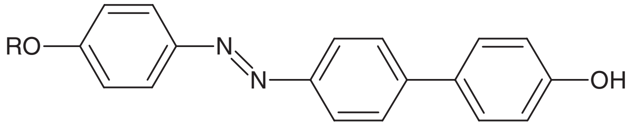


Figure 6. ^{1}H-NMR spectra of compound A_{14} (series I).



4′-[(4-*n*-alkoxyphenyl)diazenyl] biphenyl-4-ol (where $R = C_{14}H_{29}$ series I)

*4-*n*-Alkoxy Anilines.* A mixture of 4-*n*-alkoxy acetanilide (0.146 mol), water (70 ml), and concentrated HCl (45 ml) was stirred for 10–12 hr at 90°C–95°C and then cooled to room temperature. The mixture was made alkaline with 50% NaOH at 20°C. The oily product (for the lower members C_1–C_8) was extracted with ether. The ether extract was dried and concentrated at reduced pressure to give oil, which was purified by distillation. The higher members (C_{10}–C_{16}) were separated as solid and filtered directly without ether extraction. The boiling points and melting points of all the alkoxy anilines agree well with the values reported in the literature [24–26].

Diazotization of Alkoxy Aniline [27]. Alkoxy aniline (0.005 mol, 1.15 g) was taken in 50 ml of water in a beaker. It was then cooled to 0°C–5°C with ice in an ice bath. Later on, concentrated HCl (0.03 mol, 3.6 ml) was added and the reaction mixture was stirred for 1 hr. A solution of $NaNO_2$ (0.005 mol, 0.35 g) in water (5 ml) previously cooled to 0°C was then added over a period of 5 min with stirring. The solution was further stirred for another 1 hr. At this stage, Congo red paper turns blue and starch iodide paper also turns blue. It showed the positive test (i.e., the presence of nitrous acid). Then, sulfamic acid was added to remove excess of nitrous acid. At this stage, Congo red paper turns blue (positive test) and starch iodide paper had no effect (negative test). The diazonium salt was obtained as a clear solution, which was used for subsequent coupling reaction.

*Synthesis of 4′-[(4-*n*-Alkoxyphenyl)Diazenyl]Biphenyl-4-ol.* To a well-stirred solution of 4-hydroxy biphenyl (0.005 mol, 0.85 g) in water (50 ml) was added a diazonium chloride

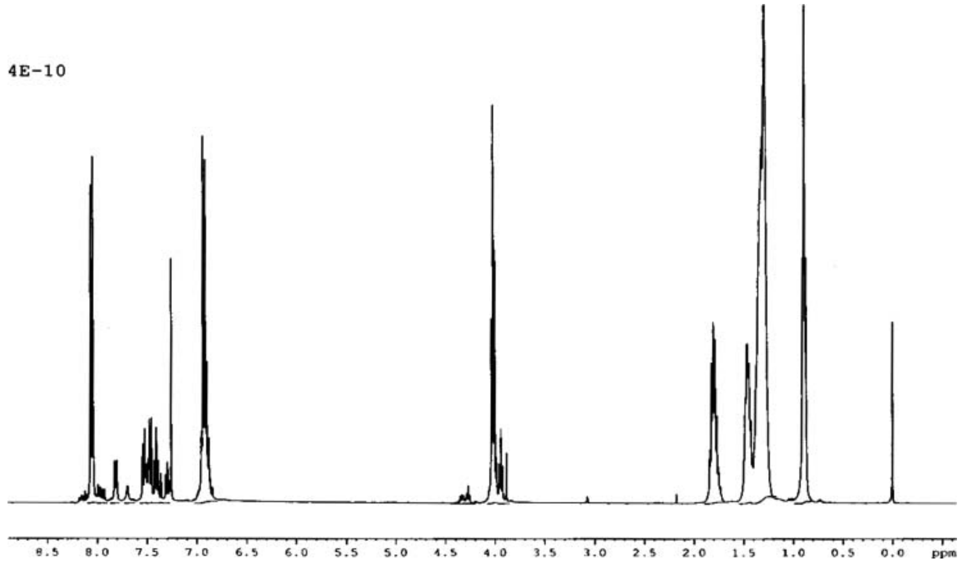
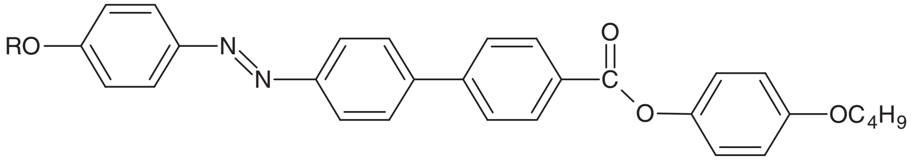


Figure 7. ^{1}H-NMR spectra of compound B_{10} (series II).



4′-[(4-*n*-alkoxyphenyl)diazenyl]4-butoxy phenyl biphenyl-4-carboxylate (where R = $C_{10}H_{21}$ series II).

of alkoxy aniline gradually for 1 hr at 0°C–5°C. The pH (7.0) was maintained by the addition of NaOH solution (10% w/v). The mixture was stirred for another 3–4 hr for complete separation and the dye was isolated by filtration, washed with water, dried, and crystallized from ethyl acetate to get orange-colored crystals. The yield was about 75%. All the compounds had been purified by column chromatography on silica gel (80–120 mesh) using a mixture of ethyl acetate/petroleum ether (7/3) as an eluent.

Data. Compound A_{10} (Series I). Yield: 73%, MP 119°C; elemental analysis for calculated C 78.10%, H 7.96%, N 6.51%; found C 78.44%, H 8.20%, N 6.02% for $C_{28}H_{34}N_2O_2$; FT-IR (KBr pallete) 3061 cm^{-1} (–C–H aromatic stretching), 2850–2920 cm^{-1} (–CH_3 aliphatic stretching), 1598 cm^{-1} (–N=N–), 1418–1481 cm^{-1} (–CH bending of CH_2), 1367–1372 cm^{-1} (–C–H bending of CH_3), 817–758 cm^{-1} (–CH bending out of plane), 723 cm^{-1} (–CH_2 rocking); ^{1}H-NMR ($CDCl_3$): 0.90 ppm (t, 3H, CH_3 of aliphatic chain), 1.28–1.85 ppm (m, 16H, –CH_2 of alkyl chain), 3.86–3.89 ppm (d, 2H, –OCH_2 of alkoxy chain), 6.09 ppm (s, phenolic –OH free), 6.81–7.29 ppm (m, 12H, Ar–H); mass (GC-MS): molecular weight of compound 486 g/mol and molecular ion peak as $(M)^+$ at 485.4 (*m*/*z*).

Series II compounds synthesized as per Scheme II.

*Synthesis of 4-*n*-Alkoxy Anilines.* 4-*n*-Alkoxy anilines were prepared as described in Series I.

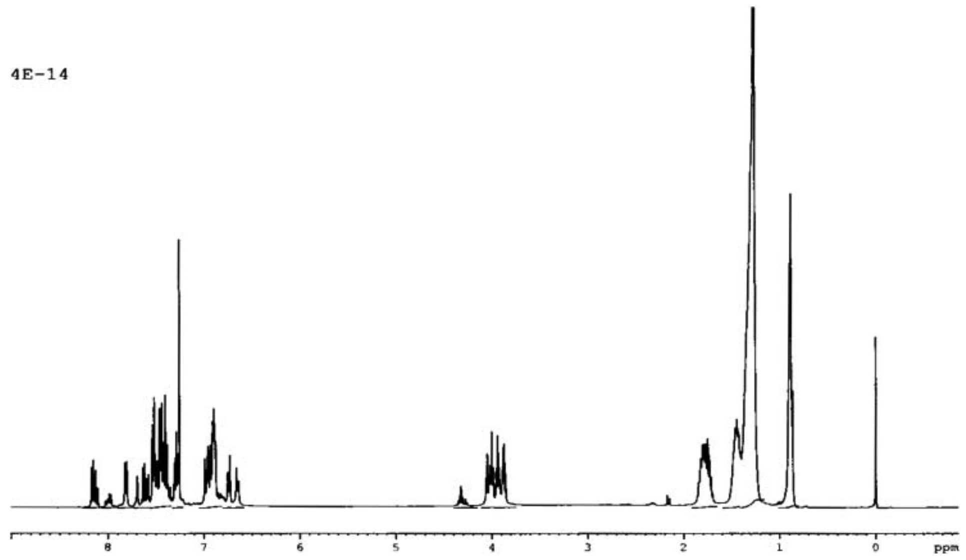
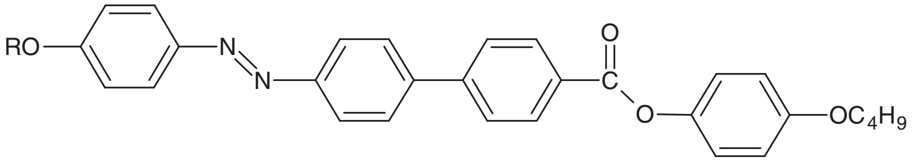


Figure 8. ^{1}H-NMR spectra of compound B_{14} (series II).



4′-[(4-*n*-alkoxyphenyl)diazenyl]4-butoxy phenyl biphenyl-4-carboxylate (where R = $C_{14}H_{29}$ series II).

Diazotization of Alkoxy Aniline. Diazotization of alkoxy aniline was carried out as described in Series I.

*Synthesis of 4′-[(4-*n*-Alkoxyphenyl)Diazenyl]Biphenyl-4-ol.* Synthesis of 4′-[(4-*n*-alkoxyphenyl)diazenyl]biphenyl-4-ol was carried out as per the procedure described in Series I.

*Preparation of 4-*n*-Alkoxy Benzoic Acid [28,29].* 4-hydroxy benzoic acid (0.1 mol, 13.8 g), corresponding *n*-alkyl bromide (0.12 mol, 23.20 ml), and KOH (0.25 mol, 14.0 g) were dissolved in methanol (lower member)/ethanol (higher member) (100 ml) in an RBF fitted with a reflux condenser and refluxed the mixture in a water bath for 8 hr. Then 10% aqueous KOH solution (25.0 ml) was added to the flask and reflux continued for 2–3 hr to hydrolyze any ester if formed. The solution was cooled to room temperature, and the reaction mixture was acidified by pouring 1:1 ice-cooled dilute HCl and water; the precipitated mass was filtered and washed by water. Then, the isolated mass was dried in a vacuum oven. The alkoxy acids were crystallized in methanol until a constant transition temperature was obtained. The transition temperature thus obtained is in good agreement with the values reported in the literature.

*Preparation of 4-*n*-Alkoxy Benzoyl Chlorides [30].* 4-*n*-alkoxy benzoic acid (0.01 mol, 2.5 g) and freshly distilled thionyl chloride (0.03 mol, 2.19 ml) were taken in an RBF attached

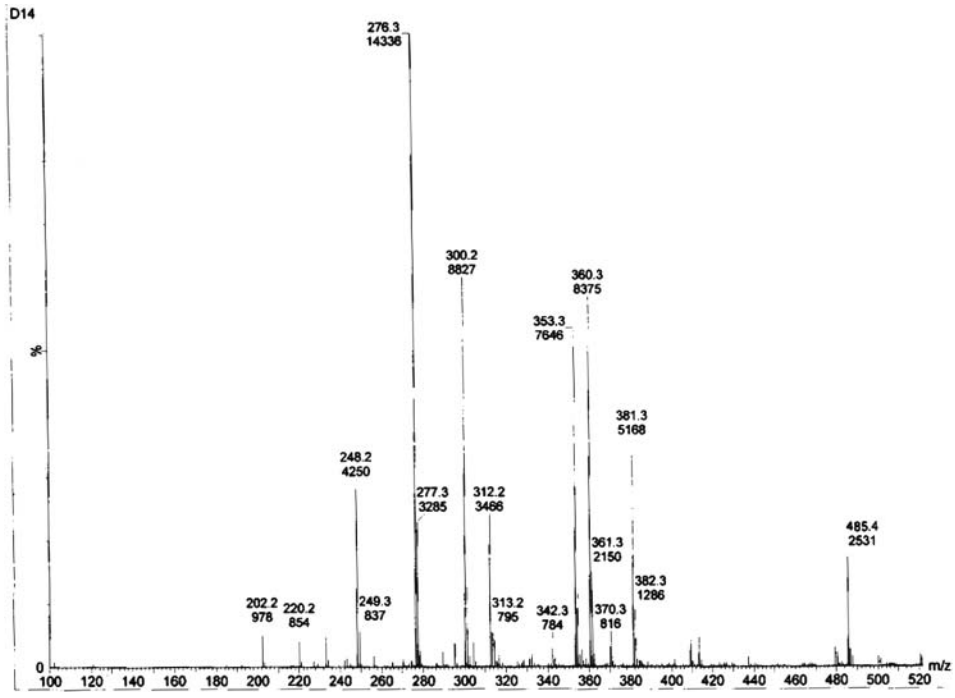


Figure 9. Mass spectra of compound A_{14} (series I).

to a reflux condenser fitted with a calcium chloride guard tube. The mixture was refluxed in a water bath till the evolution of HCl gas ceased. Excess of thionyl chloride was distilled off under pressure using a vacuum pump and the 4-*n*-alkoxy benzoyl chloride left behind was directly treated for the next reaction without further purification.

*Synthesis of 4′-[(4-*n*-alkoxyphenyl)Diazenyl]4-Butoxy Phenyl Biphenyl Carboxylate.* 4′-[(4-*n*-alkoxyphenyl)diazenyl]biphenyl-4-ol (0.002 mol, 0.86 g) was dissolved in dry pyridine (10 ml) and was added dropwise with occasionally stirring in to ice-cold 4-butoxy benzoyl chloride (0.002 mol, 0.39 g) in an RFB. Then the mixture was refluxed in a hot water bath for 2 hr and was allowed to stand for overnight. The mixture was acidified using cold 1:1 diluted HCl to precipitate the product. The solid obtained was filtered, washed successively with saturated $NaHCO_3$ solution, dilute NaOH solution, and two to three times with water; the crude solid thus obtained was purified a number of times using hot water until a constant melting temperature was obtained. The purity of all of these compounds was checked by TLC, yield in general 65%–75%. All the compounds have been purified by column chromatography on silica gel (80–120 mesh) using a mixture of ethyl acetate/petroleum ether (7/3).

Data. Compound B_{10} (Series II). Yield: 66%, MP 85°C; elemental analysis for calculated C 77.20%, H 7.64%, N 4.62%; found C 77.57%, H 7.95%, N 4.91% for $C_{39}H_{46}N_2O_4$; FT-IR (KBr pallete) 3037 cm^{-1} (–C–H aromatic stretching), 2852–2918 cm^{-1} (–CH_3 aliphatic stretching), 1687 cm^{-1} (C=O stretching), 1606 cm^{-1} (–N=N–), 1409–1469 cm^{-1}

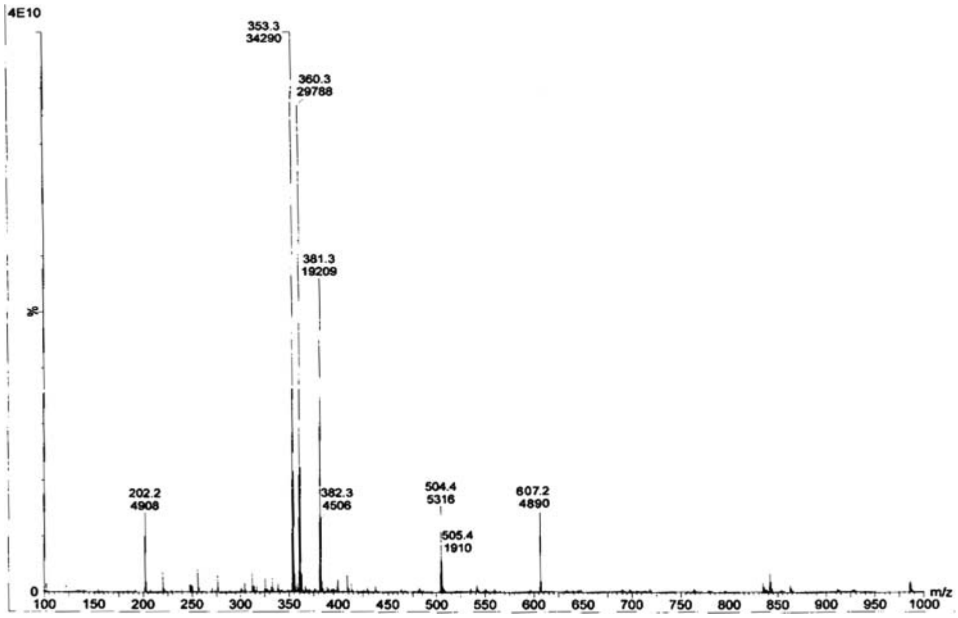


Figure 10. Mass spectra of compound B_{10} (series II).

(–CH bending of CH_2), 1370 cm^{-1} (–C–H bending of CH_3), 1255–1064 cm^{-1} (–C–O–C–stretching of alkoxy chain), 819–758 cm^{-1} (–CH bending out of plane), 717 cm^{-1} (–CH_2 rocking); ^{1}H-NMR ($CDCl_3$): 0.90 ppm (m, 6H, CH_3 of aliphatic chain), 1.29–1.83 ppm (m, 28H, –CH_2), 3.88–3.95 ppm (m, 4H, –OCH_2 of alkoxy chain), 6.87–6.95 ppm (m, 16H, Ar–H); FAB mass spectra: molecular weight of compound 606 g/mol and molecular ion peak as $(M+1)^+$ at 607.2 (*m*/*z*).

Results and Discussion

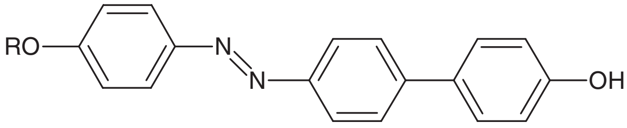
The compounds of both series are subjected to elemental analysis. The elemental analysis data agreed with theoretical values as per the expected structure. The FT-IR spectra of representative compounds are shown in Figs. 1–4. The ^{1}H-NMR spectra of representative compounds are shown in Figs. 5–8. The mass spectra of these compounds are shown in Figs. 9 and 10. The *m*/*z* ratios obtained from the spectra of representative samples are matched with their molecular ion peak. The purity of the compounds is checked by TLC. It shows one spot, indicating single compound. All the compounds were purified by column chromatography using silica gel (100–200 mesh) and ethyl acetate/petroleum ether (7:3) solvent system.

In earlier report [22], the alkoxy was prepared from azophenols using a Pd-catalyzed coupling reaction of a suitable azobenzene precursor with alkyl zinc chlorides.

In the present case, we have used alkoxy aniline containing C_1–C_8, C_{10}, C_{12}, C_{14}, and C_{16} carbon atoms in the alkoxy chain followed by diazotization with 4-hydroxy biphenyl using a classical method [31] and the mesogenic properties were investigated for these compounds.

Table 1. Transition temperature data of series I

		Transition temperature (°C)	
Code no.	R = *n*-alkyl	Sm	I
A_1	Methyl	156	182
A_2	Ethyl	150	177
A_3	Propyl	144	173
A_4	Butyl	148	160
A_5	Pentyl	130	158
A_6	Hexyl	129	155
A_7	Heptyl	130	140
A_8	Octyl	104	136
A_{10}	Decyl	72	119
A_{12}	Dodecyl	89	113
A_{14}	Tetradecyl	87	102
A_{16}	Hexadecyl	86	104



Series I

In another case, the –OH group of a biphenyl moiety is esterified by the (C_4) alkoxy acid. On the one end, the number of carbon atoms in the alkoxy chain was fixed (C_4H_9) and on the other end it was varied (C_1–C_8, C_{10}, C_{12}, C_{14}, and C_{16}); for these compounds, the mesogenic properties were also investigated.

Mesomorphic properties and thermal stability for the two new homologous series I and II were determined by a hot-stage polarizing microscope. Transition temperatures of both series are given in Tables 1 and 2.

In series I, all compounds exhibit enantiotropic smectic-A mesophase. The plot of transition temperatures versus the number of carbon atoms in the alkoxy chain (Fig. 11) exhibits no usual odd–even effect but as the series is ascended the curve shows a falling tendency.

In series II, compounds containing C_1–C_8 carbon atoms in the alkoxy chain are monotropic smectic-A liquid crystalline compounds, whereas C_{10}, C_{12}, C_{14}, and C_{16} are enantiotropic smectic-A compounds. The plot showing transition temperatures versus the number of carbon atoms in the alkoxy chain (Fig. 12) exhibits odd–even effect up to C_5 carbon atom.

The transition temperatures data obtained from a polarizing microscope are compared with differential scanning calorimetry (DSC) data and the data of some representative compounds are given in Table 3. Both the data are almost comparable. The DSC curves of compounds of series I and II are shown in Figs. 13–16.

The above two series made it possible to observe the effects of structural changes on mesomorphic behavior in a system that was studied previously.

The texture of the liquid crystalline compounds is given as microphotographs in Fig. 17.

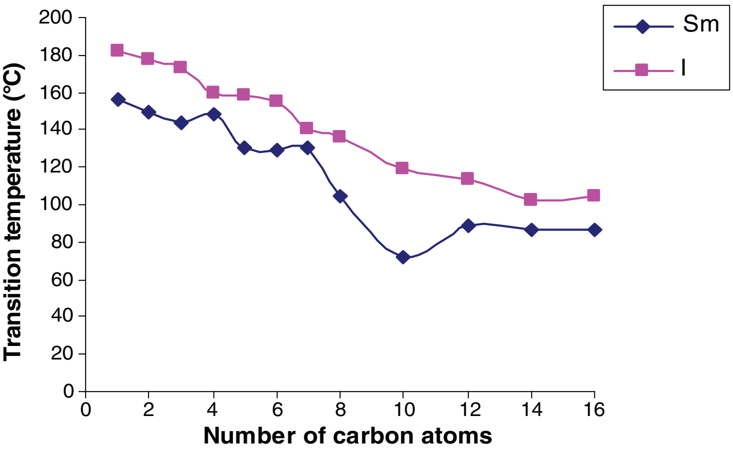


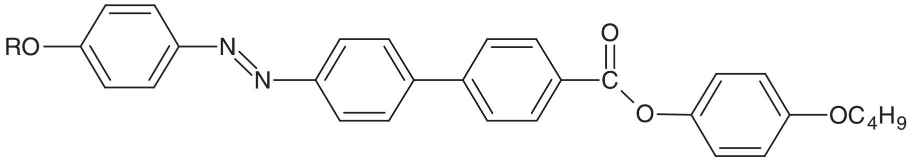
Figure 11. Transition temperature graph of series I.

It has been observed that series I compounds have high transition temperature than that of series II compounds, in spite of high molecularity of compounds. This is because of the presence of hydrogen bonding in compounds of series I as reported earlier [32]. The

Table 2. Transition temperature data of series II

		Transition temperature (in °C)	
Code no.	R = *n*-alkyl	Sm	II
B$_1$	Methyl	142^a	162
B$_2$	Ethyl	120^a	155
B$_3$	Propyl	136^a	149
B$_4$	Butyl	96^a	142
B$_5$	Pentyl	110^a	136
B$_6$	Hexyl	118^a	130
B$_7$	Heptyl	85^a	128
B$_8$	Octyl	84^a	116
B$_{10}$	Decyl	74	94
B$_{12}$	Dodecyl	80	92
B$_{14}$	Tetradecyl	100	114
B$_{16}$	Hexadecyl	82	95

[a] Monotropic phase.



Series II

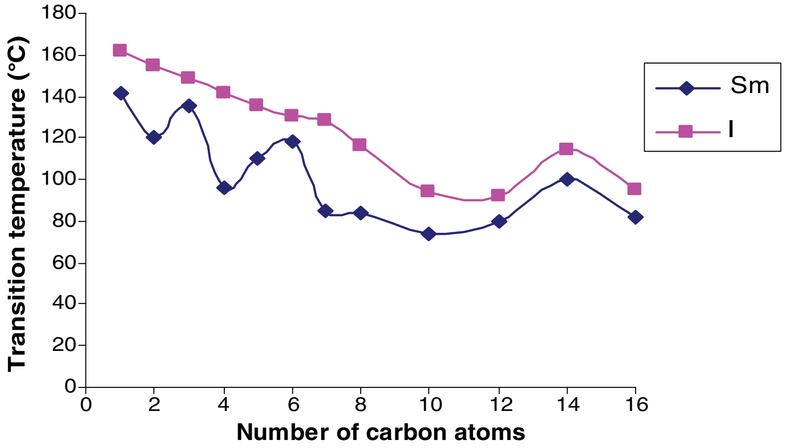
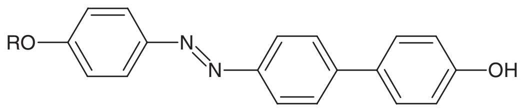
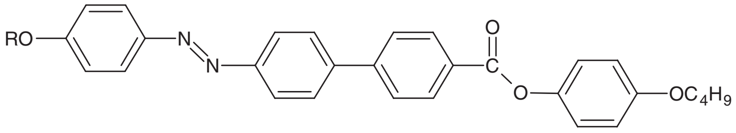


Figure 12. Transition temperature graph of series II.

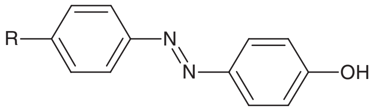
hydrogen bonding in compounds of series I is confirmed by IR spectra. The IR spectra of compounds show that the broad band centered between 3430 cm^{-1} and 3414 cm^{-1}. This band disappeared after esterification in series II. Both the series compounds show smectic-A mesophase because of the presence of a biphenyl ring due to which the lateral cohesion force is more compared with the terminal cohesion force. That is why the molecules remain in the form of lamellar bunch.



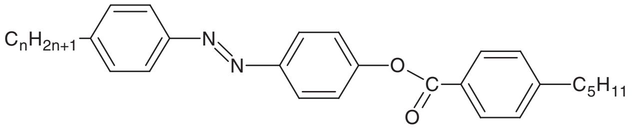
Series I



Series II



Series A



Series B

A comparison of the reported 4(4-alkyl phenylazo)phenols shows it is not mesomorphic (series A), whereas 4′-[(4-*n*-alkoxyphenyl)diazenyl]biphenyl-4-ol (series I) is mesomorphic (Table 4).

The diazotization reactions are run in aqueous solutions, and there is no difficulty for higher analogues. The present compound is smectogenic having a higher clearing temperature than that of phenol analogues.

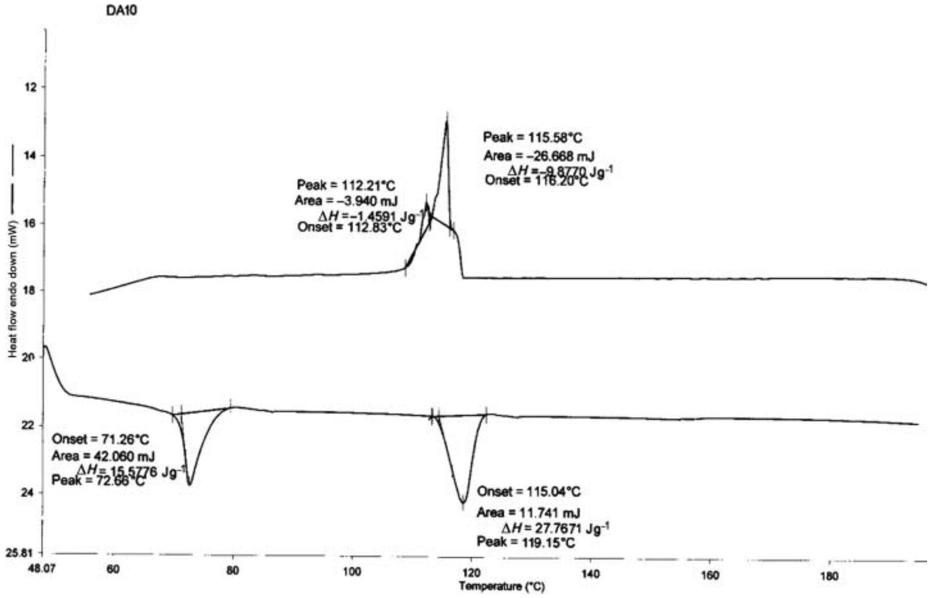


Figure 13. DSC thermogram for compound A_{10} on heating and cooling (series I).

Compounds with alkyl and alkoxy terminal groups on both sides and phenyl and biphenyl moieties in the central core and having central linkages are identical in both types of series compounds.

It has been observed that when an alkyl group is present at the terminal phenyl group, the clearing temperature is always lower than that of the alkoxy terminal group as indicated by Gray et al. [33].

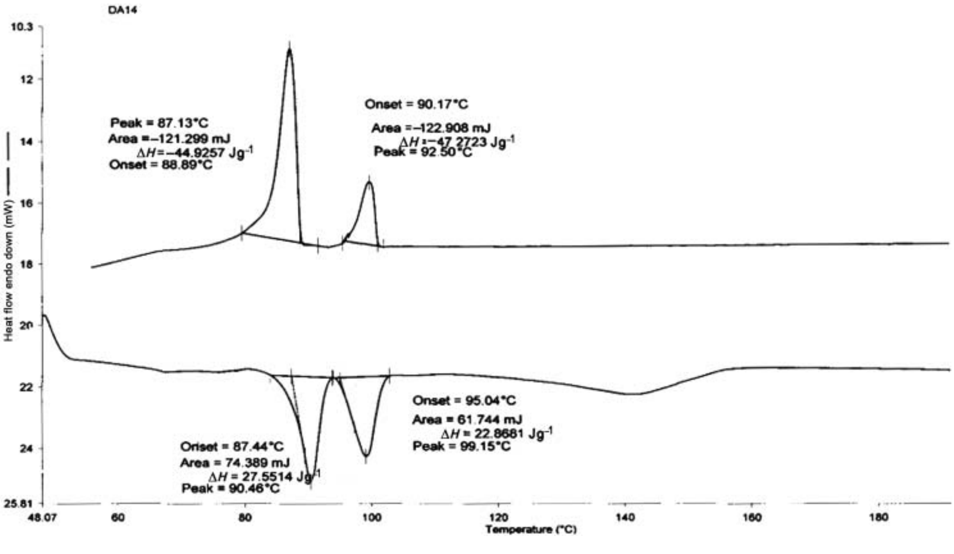


Figure 14. DSC thermogram for compound A_{14} on heating and cooling (series I).

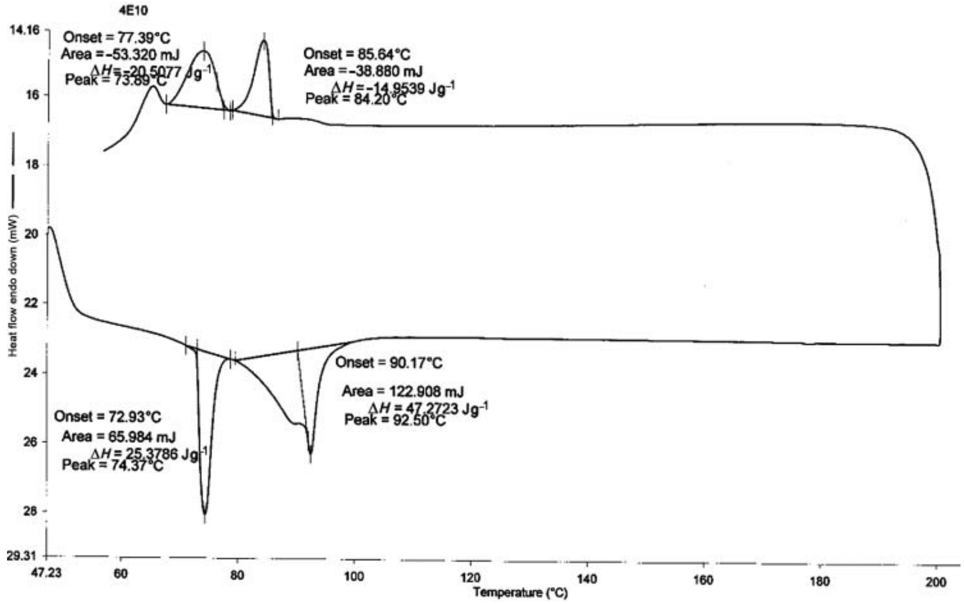


Figure 15. DSC thermogram for compound B_{10} on heating and cooling (series II).

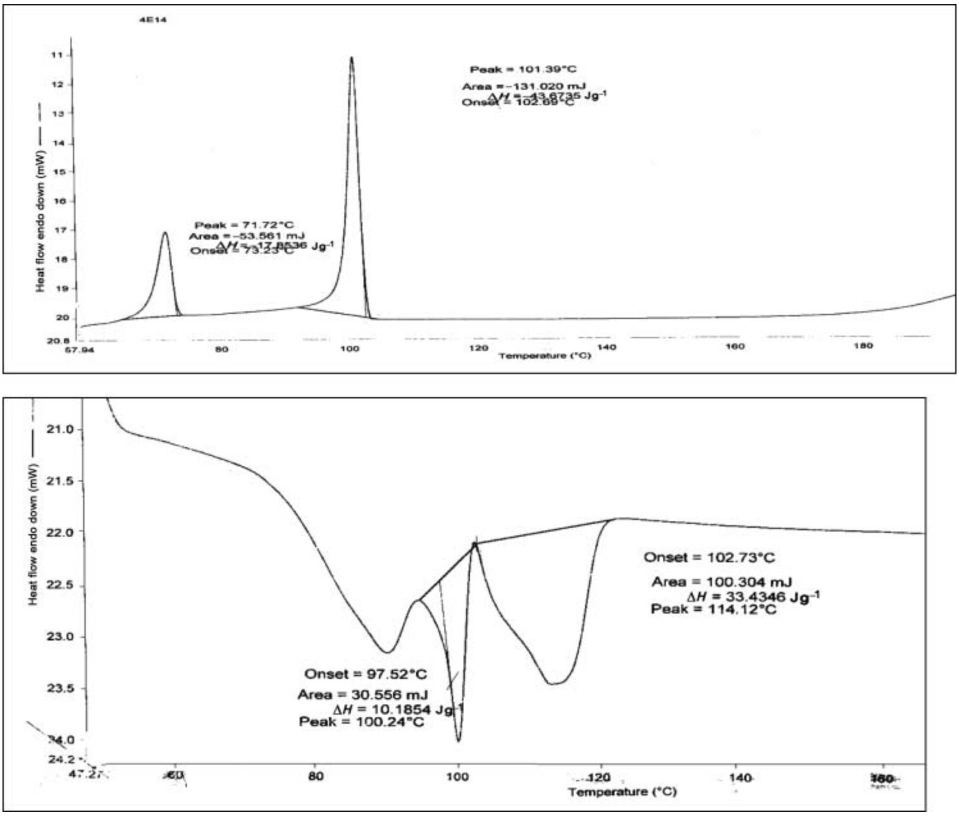
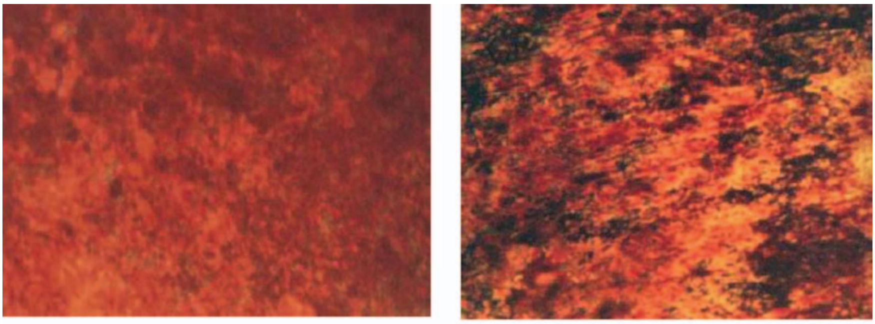
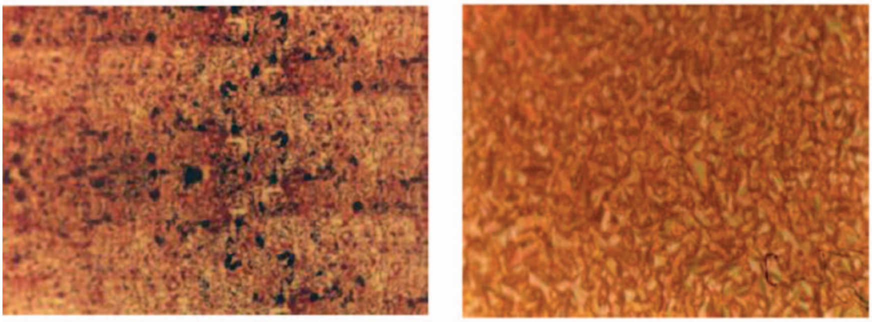


Figure 16. DSC thermogram for compound B_{10} on heating and cooling (series II).



(series I)A_{10}
Smectic-A phase at 71.26°C

(series I) A_{14}
Smectic-A phase at 87.44°C



(series II)B_{10}
Smectic-A phase at 74.73°C

(series II) B_{14}
Smectic-A phase at 100.24°C

Figure 17. Microphotographs of the compounds on heating.

The comparison of the reported 4(4-alkyl phenylazo)phenyl-4-pentylbenzoate (series B) with 4′[(4-alkoxy phenyl)diazenyl]4-*n*-butoxy phenyl biphenyl carboxylate (series II) reveals that the clearing temperatures of series B compounds are greater than those of the present series II (Tables 5 and 6). Another interesting observation seen in the above series is that when the hydrocarbon chains are connected directly to the benzene ring, the mesophase starts at lower temperatures. In series B, a nematic mesophase starts from very

Table 3. Transition temperature and DSC data of series I and II

Code no.	Transition	Peak temperature (Microscopic temperature) (in °C)	ΔH (J g^{-1})	ΔS (J g^{-1} k^{-1})
A_{10}	Cr-Sm	71.26 (72)	15.5776	0.0926
	Sm-I	119.15 (119)	27.7671	0.0406
A_{14}	Cr-Sm	90.46 (87)	27.5514	
	Sm-I	99.15 (102)	27.7671	0.2070
B_{10}	Cr-Sm	74.73 (74)	25.3786	−0.2367
	Sm-I	92.50 (94)	47.2723	−0.3153
B_{14}	Cr-Sm	100.24 (100)	10.1864	0.0780
	Sm-I	114.12 (114)	33.4346	0.1313

Table 4. Transition temperature data of series A and I

Series A		Series I	
n (number of carbon atoms)	Isotropic (°C)	*n* (number of carbon atoms)	Isotropic (°C)
8	76	1	182
10	77	2	177
12	87	3	173
14	91	4	160
16	98	5	158
18	100	6	155
20	104	7	140
22	–	8	136
–	–	10	119
–	–	12	113
–	–	14	102
–	–	16	104

first member of the carbon chain, while smectic-C mesophase starts from higher homologues say C_{14}. In the present series II, the clearing temperatures are lower than those of series B. For the first carbon atom up to C_{16} carbon atom in the alkyl chain, smectic-A mesophase was obtained because both ends of the series have alkoxy groups and the middle core of the series has a biphenyl moiety, which increases the polarizability of the molecule. As a result of this, the molecule becomes more lamellar, stratified, and highly arranged, thus showing smectic-A phase.

Conclusion

All the compounds of series I exhibit mesomorphic behavior showing enantiotropic smectic-A phase. From the comparison of series I and II, it has been observed that the transition temperature of series I compounds is higher than that of series II, which is due to hydrogen

Table 5. Transition temperature data of series B and series II

n (number of carbon atoms)	Smectic-C	Nematic	Isotropic
2	–	120	207.41
4	–	84	200.1
6	–	76	187.7
8	–	80	177.6
10	–	86	169.1
12	–	79	159.1
14	80.0 (Sm-C)	84.7	153.1
16	84.0 (Sm-C)	89.2	146.4
18	86.0 (Sm-C)	93.3	140.7
20	90.0 (Sm-C)	96.5	135.5
22	86.0 (Sm-C)	100.9	130.5

Table 6. Transition temperature data of series II

n (number of carbon atoms)	Smectic A	Isotropic
1	142	162
2	120	155
3	136	149
4	96	142
5	110	136
6	118	130
7	85	128
8	84	116
10	74	94
12	80	92
14	100	114
16	82	95

bonding present in series I. In series II, mesomorphic compounds show smectic-A phase from C_1 to C_8 and hence are monotropic, whereas C_{10}, C_{12}, C_{14}, and C_{16} are enantiotropic. Both series are smectogenic because of the presence of a biphenyl moiety in the central core.

Acknowledgments

We are grateful to Prof. R. A. Vora, retired Prof. and Head, Department of Applied Chemistry, Faculty of Technology and Engineering, Kalabhavan, M. S. University of Baroda, Vadodara, India, for his valuable suggestions. We are also thankful to CDRI, Lucknow, Atul Industries Ltd., and SAIF Chandigarh for providing facilities such as elemental analysis, FT-IR, ^{1}H-NMR, mass spectral, and thermal analyses.

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