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Mesogenic Benzothiazole Derivatives with a Polar Nitro Substituent[†]

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Two new mesogenic homologous series containing 6-nitrobenzothiazole moiety at the terminus of the molecule, viz 2-(4′-n-alkoxyphenylazo)-6-nitrobenzothiazoles and 2-[4′-(4”-n alkoxybenzoyloxy) phenylazo]-6-nitrobenzothiazoles were synthesized. The molecular structures of these new compounds of both the series have been characterized by elemental analysis, FTIR, and NMR spectral studies. The mesomorphic behavior has been studied using mainly polarized microscopy and in some cases differential scanning calorimetry as well. All the nine compounds of the series I are mesogenic and exhibit only the smectic A mesophase. In series II, all the twelve members synthesized exhibit enantiotropic mesomorphism. This series exhibits enantiotropic nematic mesophase from methoxy to n-heptyloxy derivatives. The smectic C mesophase commences from methoxy derivative, and persist up to n-butyloxy derivative, whereas the smectic A mesophase enters from the n-butyloxy derivative, and remains up to the last member synthesized. The mesomorphic properties of the present series are compared with other structurally related series to evaluate the effect of the benzothiazole ring and the polar nitro substituent on mesomorphism.

Keywords: 6-Nitrobenzothiazole; azomesogens; nematic; smectic A; smectic C

INTRODUCTION

The liquid crystalline properties of organic compounds are mainly depends on the mesogenic core structure, it’s geometry, polarizability ratio, lateral to terminal attractive force ratio, the length to breadth ratio, etc. [1].

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Until 1983, it was generally accepted that lateral substituent reduce or diminish the mesogenic property of a compound, and the extent of the effect depends on the size of lateral substituent by disrupting the molecular packing. Many researchers studied the mesogenic properties of lateral substituted homocyclic compounds, and they have established the relation for the effect of different lateral substituents on the mesogenic properties. Wide ranges of different lateral substituents (e.g., -F, -Cl, $-NO_2$, $-CH_3$, $-CF_3$) have been incorporated into many liquid crystal systems in different environments. With the aim of regulating the parameters of the liquid crystal, the meso state has been widely studied, and definite data have already been accumulated on the change of properties of a liquid crystal depending on the type and position of a substituent [2–4].

Liquid crystals containing a heterocyclic ring system have also been attracting attention in their own right. These kinds of mesogens exhibit interesting properties [5], such as lower symmetry and different polarizability as compared to the homocyclic unit. In addition to this, it possesses an additional permanent dipole moment, that affects the magnitude and direction of the total molecular dipole moment without increasing the molecular breadth [6].

Many mesogenic compounds containing a heterocyclic ring have been reported in the literature. Single ring heterocyclic moieties such as pyridine [6–8], furyl [6], substituted pyrimidine carboxylic acid [9], thiazole [10], thiadiazole [11–14], and oxadiazole [13] are reported in the literature. Barbera et al. [15] have synthesized 2-pyrazoline derivatives and also studied the optical, NLO and mesogenic properties of such materials. Highly polar thiophene based liquid crystals have also been reported [16] in the literature. However, fused ring heterocyclic derivatives, which are two condensed rings, are practically planar and rigid molecule. Liquid crystals containing fused heterocyclic ring system such as coumarin [17] mesogens containing azo central linkage, thiazole[5,4-d]thiazoles [18], imidazo[2,1-b]-1,3,4-thiadiazoles [19], and Isocoumarin [20] derivatives having central ester and amide linkage exhibiting smectic C and nematic mesophase, and very high mesophase transition temperatures are reported in the literature. Esters of 7-decanoyloxychromone-3-carboxylic acid [21,22], flavone [23] has also been reported. Recently Xuelong et al. [24] synthesized and studied the mesogenic properties of benzo-2, 1-3-thiadiazole derivatives.

Pavluchenko et al. [25] reported mesogens containing benzothizole and benzoxazole with different central linkages and different lateral substitution at different positions so as to evaluate the effect of structural changes on mesomorphic properties. They observed that the substitution at sixth position was thermally more stable as compared to that of the fifth position on the benzothiazole ring. They have also concluded that the 6-substitued benzothiazoles in comparison with their benzoxazole analogs has greater mesophase transition temperatures because of the difference in degree of aromatization of azole cycles that is degree of conjugation of heteroatom *p*-electrons with π-electrons of cycle.

Recently, we reported two mesogenic homologous series of each containing 6-chloro benzothiazole [26] and 6-methoxybenzothiazole [27] ring systems with azo and/or ester central linkage. In order to study more about the effect of benzothiazole ring and nitro substituent on mesomorphic properties in such systems, we have synthesized two new extensive mesogenic homologous series of benzothiazole derivatives containing 6-nitro substituents.

EXPERIMENTAL

Characterization

The structures of the compounds were confirmed by IR spectroscopy via KBr pellet, using a Shimadzu IR-408 spectrophotometer. ^{1}H NMR spectra were obtained with a Bruker Dpx 200 spectrometer or Bruker 300, using tetramethylsilane (TMS) as an internal reference standard. The chemical shifts are quoted as δ (parts per million) downfield from reference. CDC_{l3} was used as a solvent. The liquid crystalline properties of the mesogens were investigated on Leitz Laborlux 12 POL microscope provided with heating stage. The enthalpies of transitions reported as J/g were determined from thermograms obtained on a Universal V3 · 0G TA instrument adopting rate of 5°C/min. The calorimeter was calibrated using pure indium as standard. The purity of the final products was confirmed by thin layer chromatography and microanalysis performed on a Perkin–Elmer series 2400 elemental analyzer.

Materials

4-Hydroxybenzoic acid, 4-methoxybenzoic acid, 1-bromoalkanes, thionyl chloride, anhydrous potassium carbonate, sodium nitrite, 4-nirtoaniline, potassium thiocyanate, bromine liquid and phenol, etc. were used as received. Column chromatography was done on Acme's Silica Gel (100–200 mesh). Solvents were dried and distilled prior to use.

Synthesis

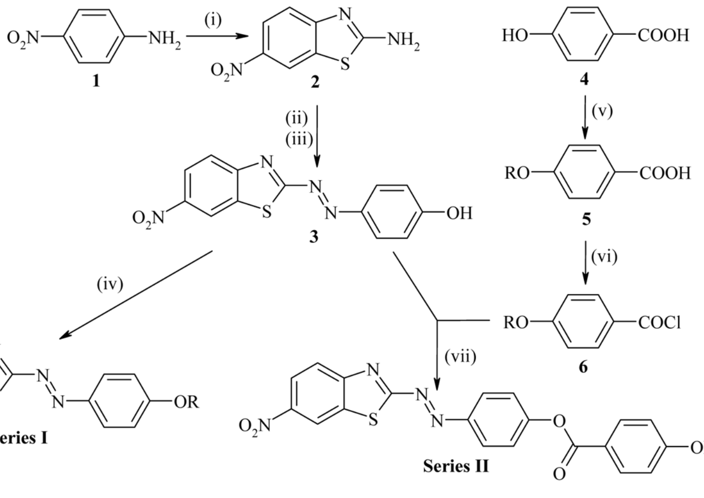
The synthetic route to series I and II is illustrated in Scheme 1.

2-Amino-6-nitrobenzothiazole [2]

2-Amino-6-nitrobenzothiazole was prepared from 4-methoxyaniline [**1**] by the reported method [28]. Crystallization from 1:1 aqueous ethanol afforded pure yellow needles of [**2**]. Yield: 73%. M.P.: 246°C (Reported [28] m.p.: 247–249°C).

2-(4′-Hydroxyphenylazo)-6-nitrobenzothiazole [3]

This was synthesized by diazotization of compound [**2**] and coupling with phenol by following the method reported by Johari and Varshney [29]. The dye thus obtained was crystallized several times using alcohol until constant melting point was obtained. Yield: 53%. M.P.: 203°C. Elemental analysis found C 51.74, H 3.08, N 18.34, $C_{13}H_8N_4O_3S$ requires C 52.00, H 2.69, N 18.66%. The IR spectrum showed a broad peak of intermolecularly hydrogen bonded, phenolic -OH between 3200–3600 cms$^{-1.}$ Other signals observed were at 3046 ($\nu_{\text{C-H,}}$ aromatic), 2922 ($\nu_{\text{C-H,}}$ aliphatic), 1603 (-N$=$N-), 1496, 1056 (Benzothiazole), 1027, 827, 635 (C-S-C) cm^{-1}.



SCHEME 1 Synthetic route to series I and II. Reagents and conditions: (i) KSCN, Br_2, AcOH; (ii) $NaNO_2$, H_2SO_4, 0–5°C; (iii) phenol, 10% NaOH (aq.), 0–10°C; Hcl; (iv) RBr, K_2CO_3, acetone; Series I: R$=$-C_nH_{2n+1}, n$=$4–8, 10, 12 and 16; (v) RBr, KOH, Ethanol; (vi) $SOCl_2$ (Excess); (vii) pyridine; 0–10°C; Hcl; Series II: R$=$-C_nH_{2n+1}, n$=$1–8, 10, 12, 14, and 16.

2-(4′-n-Alkoxyphenylazo)-6-nitrobenzothiazoles [I]

These were synthesized by alkylation of dye [**3**] using the reported method of Vyas and Shah [30]. 2-(4′-Hydroxyphenylazo)-6 nitro benzothiazole (0.1 mol), appropriate 1-bromoalkane (0.12 mol) and anhydrous potassium carbonate (0.15 mol) were added to dry acetone (60 ml). The reaction mixture was refluxed on a water bath for eight to ten hours. Completion of the reaction was checked by thin layer chromatography (TLC) (10% ethyl acetate: hexane). The reaction mixture was added to ice-cold water. The crude solid product thus obtained was triturated with cold 5% aqueous sodium hydroxide solution for 30 min so as to remove unreacted azo dye and was washed with water. The product obtained was purified by column chromatography using silica (100–200 mesh size) and 3% ethyl acetate-petroleum ether (60–80) as eluent. The compound obtained was finally crystallized using ethanol. Yield: 68–73%. The elemental analysis of all the compounds of series I was satisfactory, and results are listed in Table 1.

TABLE 1 Elemental Analysis for Series I and II Compounds

			% Required (% Found)		
Compound	R=-C_nH_{2n+1} *n*	Formula	C	H	N
Series I					
1	4	$C_{17}H_{16}N_4O_3S$	57.29 (57.43)	4.52 (4.36)	15.72 (15.59)
2	5	$C_{18}H_{18}N_4O_3S$	58.36 (58.08)	4.90 (4.74)	15.12 (15.23)
3	6	$C_{19}H_{20}N_4O_3S$	59.36 (59.61)	5.24 (5.08)	14.57 (14.18)
4	7	$C_{20}H_{22}N_4O_3S$	60.28 (60.36)	5.56 (5.93)	14.06 (14.27)
5	8	$C_{21}H_{24}N_4O_3S$	61.14 (60.58)	5.86 (5.67)	13.58 (13.82)
6	10	$C_{23}H_{28}N_4O_3S$	62.70 (62.25)	6.41 (6.80)	12.72 (13.10)
7	12	$C_{25}H_{32}N_4O_3S$	64.08 (63.82)	6.88 (6.06)	11.96 (11.54)
8	14	$C_{27}H_{36}N_4O_3S$	65.29 (65.60)	7.31 (7.14)	11.28 (11.58)
9	16	$C_{29}H_{40}N_4O_3S$	66.38 (66.73)	7.68 (7.40)	10.68 (10.43)
Series II					
10	1	$C_{21}H_{14}N_4O_5S$	58.06 (58.43)	3.25 (2.80)	12.90 (13.41)
11	2	$C_{22}H_{16}N_4O_5S$	58.92 (59.06)	3.60 (3.88)	12.49 (12.07)
12	3	$C_{23}H_{18}N_4O_5S$	59.73 (59.41)	3.92 (3.67)	12.11 (12.45)
13	4	$C_{24}H_{20}N_4O_5S$	60.49 (60.12)	4.23 (4.59)	11.76 (11.98)
14	5	$C_{25}H_{22}N_4O_5S$	61.21 (61.59)	4.52 (4.83)	11.42 (10.95)
15	6	$C_{26}H_{24}N_4O_5S$	61.89 (62.28)	4.79 (4.38)	11.10 (11.32)
16	7	$C_{27}H_{26}N_4O_5S$	62.53 (62.21)	5.05 (5.39)	10.80 (11.25)
17	8	$C_{28}H_{28}N_4O_5S$	63.14 (63.57)	5.30 (4.94)	10.52 (10.87)
18	10	$C_{30}H_{32}N_4O_5S$	64.27 (63.77)	5.75 (6.06)	09.99 (09.63)
19	12	$C_{32}H_{36}N_4O_5S$	65.28 (65.36)	6.16 (6.37)	09.52 (09.84)
20	14	$C_{34}H_{40}N_4O_5S$	66.21 (65.94)	6.54 (6.13)	09.08 (09.40)
21	16	$C_{36}H_{44}N_4O_5S$	67.05 (67.41)	6.88 (7.30)	08.69 (08.82)

IR and ^{1}H NMR spectral data of n-tetradecyloxy derivative as representative member are given below.

2-(4′-n-Tetradecyloxyphenylazo)-6-nitrobenzothiazole

IR spectrum (KBr) ν_{max}/cm^{-1}: 3051($\nu_{C\text{-}H,}$ aromatic), 2915($\nu_{C\text{-}H,}$ aliphatic), 2849, 2243, 1603 (-N = N-), 1573, 1473, 1436, 1256 (Aryl ether), 1058 (Benzothiazole), 1029, 849, 636(C-S-C) cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$, 200 MHz): δ 8.81 (d, $J_{7,5} = 2.1$ Hz, 1H, ArH at C-7), 8.35–8.41 (dd, $J_{5,7} = 2.1$ Hz, $J_{5,4} = 9.2$ Hz, 1H, ArH at C-5), 8.23 (d, $J = 9.2$ Hz, 1H, ArH at C-4), 8.10 (d, $J = 8.6$ Hz, 2H, ArH at C-2′ and C-6′), 7.06 (d, $J = 9.0$ Hz, 2H, ArH at C-3′ and C-5′), 4.11 (t, 2H, Ar-O-CH_2), 1.85 (m, 2H, Ar-O-C-CH_2), 1.27–1.55(m, 22H, 11 × CH_2), 0.88 (t, 3H, CH_3).

4-n-Alkoxybenzoic Acids [5] and 4-n-Alkoxybenzoyl Chlorides [6]

These were synthesized by the modified method of Dave and Vora [31].

2-[4′-(4″-n-Alkoxybenzoyloxy) Phenylazo]-6-nitrobenzothiazoles [II]

The compound [**3**] (0.02 mol) was dissolved in dry pyridine (5 ml), and a cold solution of 4-*n*-alkoxybenzoyl chloride [6] (0.02 mol) in dry pyridine was added with stirring in an ice bath. The mixture was allowed to stand overnight at room temperature. It was acidified with cold 1:1 aqueous hydrochloric acid. The solid obtained was separated, dried, and triturated by stirring for 30 min with 5% aqueous sodium hydroxide solution and was washed with water. The insoluble mass separated was crystallized several times from acetic acid until constant transition temperatures were obtained. Yield 59–64%. The elemental analysis of all compounds of series II was satisfactory, and results are listed in Table 1. IR and ^{1}H NMR spectral data of *n*-tetradecyloxy derivatives as representative member are given below.

2-[4′-(4″-n-Tetradecyloxybenzoyloxy) Phenylazo]-6-nitrobenzothiazole

IR spectrum (KBr) ν_{max}/cm^{-1}: 3091 ($\nu_{C\text{-}H,}$ aromatic), 2921 ($\nu_{C\text{-}H,}$ aliphatic), 2870, 1728 (-COO-), 1605 (-N = N-), 1578, 1514 (Ar-NO_2), 1470, 1345, 1039 (Benzothiazole), 894, 848, 646 (C-S-C). ^{1}H NMR spectrum ($CDCl_3$, 200 MHz): **δ** 8.87 (d, $J = 2.3$ Hz, 1H, ArH at C-7) 8.41 (dd, $J_{5,7} = 2.3$ Hz, $J_{5,4} = 8.9$ Hz, 1H, ArH at C-5), 8.31 (d, $J = 8.9$ Hz, 1H ArH at C 4), 8.16–8.25 (m, 4H, ArH at C-2′, C-6′, C-2″, and C-6″), 7.51 (d,

$J = 8.8$ Hz, 2H, ArH at C 3′ and C-5′), 7.01(d, $J = 9$ Hz, 2H, ArH at C-3″ and C-5″), 4.08 (t, 2H, Ar-O-CH_2), 1.85 (m, 2H, Ar-O-C-CH_2), 1.22–1.58 (m, 22H, $11 \times CH_2$), 0.90 (t, 3H, -CH_3).

RESULTS AND DISCUSSION

Microscopic Observation and DSC for Series I and II

The mesophase exhibited by series I and II compounds are identified by examining the thin film of a sample sandwiched between a glass slide and cover slip. On cooling the isotropic liquid in an ordinary slide, polygonal or focal-conic textures characteristic of SmA phase were observed for compounds of series I. Compounds of series II, on cooling from isotropic liquid, methoxy to *n*-heptyloxy derivatives exhibit the schlieren texture of the nematic phase, which on further cooling for $n \leq 3$ exhibit the schlieren texture of SmC mesophase, whereas for $n \geq 4$ showed the focal conic texture of SmA mesophase. Only in case of *n*-butyloxy derivative, on further cooling the focal conic texture of SmA changes to the schlieren texture of SmC mesophase. Higher members ($n \geq 8$) on cooling from isotropic liquid showed only the focal-conic texture characteristic of SmA mesophase. Transition temperatures obtained for both the series are recorded in Tables 2 and 3, respectively (enantiotropic phase temperatures are recorded in the heating cycle).

Calorimetry is a valuable method for the detection of phase transition. Conclusions may be drawn concerning the nature of the phases, which participate in the transition with the help of calorimetric studies. In the present study, enthalpies of few compounds of series I and II were measured by differential scanning calorimetry. Data

TABLE 2 Transition Temperatures (°C) of the Series I Compounds

Compound no.	R=-C_nH_{2n+1} *n*	Cr		SmA		I
1	4	●	165	●	201	●
2	5	●	169	●	204	●
3	6	●	163	●	200	●
4	7	●	160	●	198	●
5	8	●	160	●	195	●
6	10	●	159	●	193	●
7	12	●	156	●	194	●
8	14	●	151	●	196	●
9	16	●	149	●	196	●

TABLE 3 Transition Temperatures (°C) of the Series II Compounds

Compound no.	R = -C_nH_{2n+1} n	Cr		SmC		SmA		N		I
10	1	●	136	●	266	—	—	●	326	●
11	2	●	134	●	261	—	—	●	325	●
12	3	●	126	●	258	—	—	●	317	●
13	4	●	121	●	151	●	255	●	314	●
14	5	●	148	—	—	●	263	●	309	●
15	6	●	146	—	—	●	276	●	308	●
16	7	●	147	—	—	●	282	●	303	●
17	8	●	161	—	—	●	294	—	—	●
18	10	●	154	—	—	●	285	—	—	●
19	12	●	151	—	—	●	277	—	—	●
20	14	●	155	—	—	●	266	—	—	●
21	16	●	142	—	—	●	263	—	—	●

are recorded in Table 4. Enthalpy values of the phase transitions agree well with the existing literature value [32], which has helped in further confirmation of the mesophase type.

The Phase Behaviour of Series I and II

Series I: 2-(4′-n-Alkoxyphenylazo)-6-nitrobenzothiazoles

All the nine compounds of series I are mesogenic and exhibit only the SmA mesophase. The transition temperatures are recorded in Table 2. The plot of transition temperatures against the number of carbon atom in the alkoxy chain (Fig. 1) show falling tendency for SmA-I transition and also exhibit usual odd–even effect for lower members. Gray [1] has explained that the terminal intermolecular attractions are playing a part in determining the Sm-I transition temperatures, i.e., the destruction of the smectic molecular order is determined by the fact that the terminal attractions are becoming

TABLE 4 DSC Data for Series I and II Compounds

Series	n	Transition	Peak temp. (°C)	$\Delta H/Jg^{-1}$	$\Delta S/Jg^{-1}K^{-1}$
I	8	Cr-Sm A	159.4	15.64	0.03616
		Sm A-I	193.5	0.78	0.0017
	14	Cr-Sm A	152.1	22.64	0.0532
		Sm A-I	195.7	01.22	0.0026
II	14	Cr-Sm A	155.9	15.00	0.0438
		Sm A-I	—	†	—

†Enthalpy could not be measured.

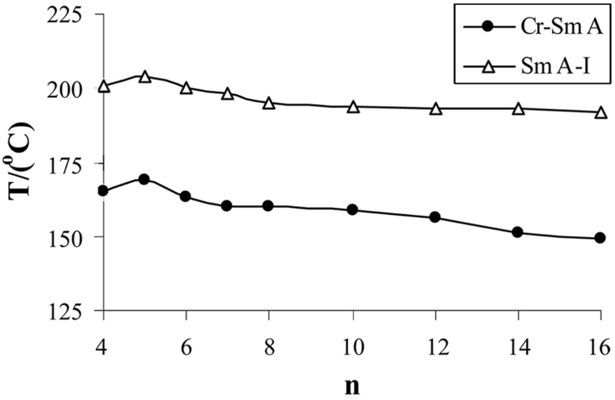


FIGURE 1 The phase behavior of series I.

weaker, so allowing partial interpenetration of the layers to occur more easily as the alkyl chains grow longer, which diminishes the SmA-I transition. This explains the falling SmA-I transition temperature curve. Cr-SmA transition exhibit falling tendency as the series ascended except the ethyloxy derivative.

Series II: 2-[4′-(4″-n-Alkoxybenzoyloxy) Phenylazo]-6-nitrobenzothiazoles

All the 12 members synthesized exhibit enantiotropic mesomorphism. The series exhibits enantiotropic nematic mesophase from methoxy to *n*-heptyloxy derivatives. The SmC mesophase commences from the methoxy derivative and persists up to *n*-butyloxy derivative whereas the SmA mesophase begins from the *n*-butyloxy derivative, which remains up to the last member synthesized. Transition temperatures were recorded in Table 3. The plot of transition temperatures against number of carbon atoms in the alkoxy chain (Fig. 2) shows a smooth falling tendency for N to I, SmC to N, SmA to I transitions. The N to I transition also exhibits the usual odd–even effect for lower members. The SmA to N transition temperatures exhibit a rising tendency as series ascended.

Mesogenic Properties and Molecular Constitution

There is close relation between mesomorphism and molecular constitution of organic compounds. Hence, transition temperature and mesophase length; measures of mesomorphism can be correlated with the molecular constitution of the compounds.

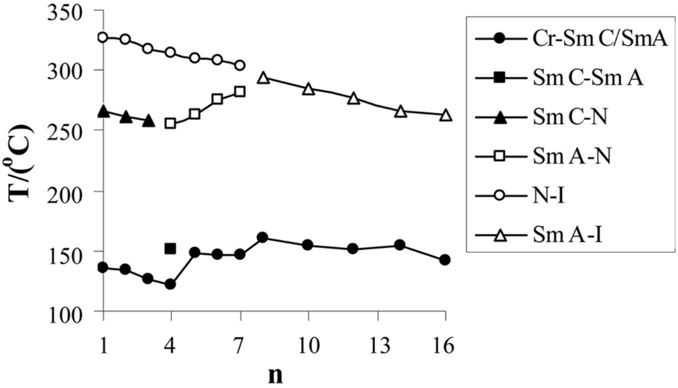


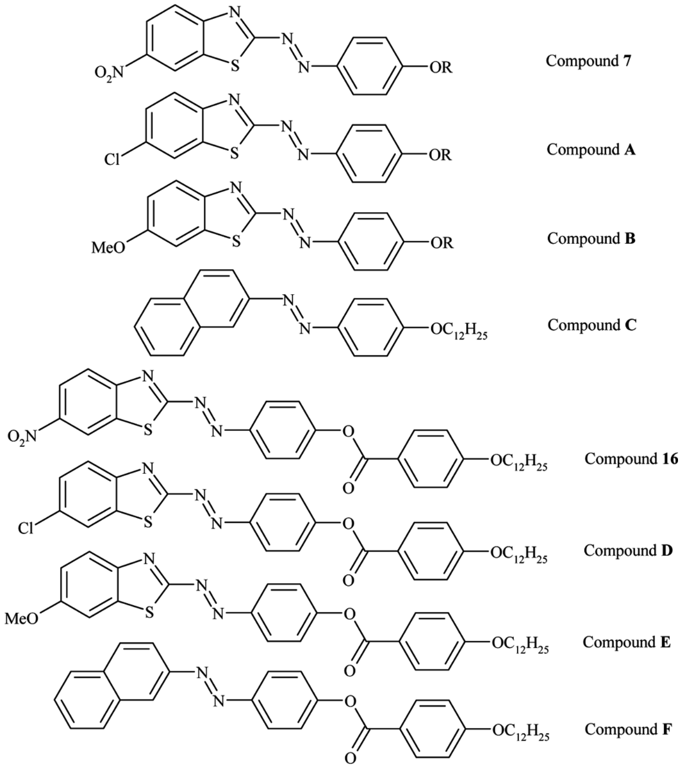
FIGURE 2 The phase behavior of series II.

Table 5 shows the comparison of transition temperatures, range (width) of mesophase phase, and thermal stabilities and molecular structures of representative compounds **7** ($n = 12$) and **16** ($n = 12$) of the present series I and II with other structurally related compounds **A** [26], **B** [27], **C** [33], **D** [26], **E** [27], and **F** [33] reported in the literature. Both compounds **7** and **A** exhibit an enantiotropic smectic mesophase. The smectic mesophase range of compound **7** is lower by 54°C, whereas the smectic thermal stability is higher by 22°C than compound **A**. Reference to molecular structure indicates that both compounds have different substituent at the sixth position of benzothiazole moiety. Compound **7** has the -NO_2 group, whereas compound **A** has the -Cl group at the sixth position of benzothiazole moiety. The higher smectic thermal stability of the mesogen **7** may be because of the C-NO_2 bond, which has greater polarizability compared to the C-Cl bond [1]. Gray [1] has explained that the dipole moment is an important factor as far as relative thermal stability of smectic phase is concerned, and the size effect is not prominent in such cases.

Table 5 indicates that compound **B** exhibits an enantiotropic nematic mesophase along with a monotropic SmA mesophase, whereas compound **7** exhibits only an enantiotropic SmA mesophase. The smectic mesophase length and thermal stability of compound **7** are higher by 31°C and 86°C, respectively than compound **B**. This may be due to the presence of C-NO_2 bond, which increases the molecular polarizability and possibly also the molecular dipolarity as compared to less dipolar -OCH_3 group. This is also reflected in comparison of compound **A** with compound **B**. The smectic mesophase length and smectic thermal stability of compound **A** is higher by 85°C and 64°C,

TABLE 5 The Comparison of Mesophase Length (°C), Thermal Stabilities (°C), and Molecular Structure of Compounds **7**, **16**, **25**, **37**, **49**, **61**, **A**, and **B**

Compound no.	Mesophase length		Thermal stability		Commencement of smectic phase
	N	Sm	N	Sm	
7	—	38	—	194	C_4
A	—	92	—	172	C_5
B	22	7	133	108	C_{12}
C	—	—	—	—	—
16	—	126	—	277	C_1
D	04	149	268	264	C_1
E	123	—	254	—	—
F	68	23	201	112	C_{10}



respectively, than compound **B** because of the presence of the more polar lateral -Cl group in compound **A**, whereas compound **B** has the less polar -OCH_3 group at the lateral position.

Table 5 shows that compound **C** is nonmesogenic, whereas compound **7** is mesogenic and exhibits an enantiotropic smectic mesophase. Reference to the molecular structure shows that compound **C** differs only at one terminus from compound **7**. Compound **7** has 6-nitrobenzothiazole ring at the terminus instead of naphthalene ring of compound **C**. Presence of lateral -NO_2 group in compound **7**, increases the overall molecular breadth. Gray [1] has explained that increase in the breadth of the molecule reduces both nematic and smectic mesophase thermal stability, but due to the presence of terminal benzothiazole ring which increases overall polarizability of the molecule with lowering the symmetry of the molecule as compared to phenyl/naphthyl derivatives and provide higher thermal stability [25]. Moreover, the polar nature of the nitro group also increases the overall polarizability of the molecules. All these factors are responsible for the mesogenic behavior of compound **7**. The same observation reflected in the comparison of compound **A** and **B** with compound **C**.

Reference to Table 5 indicates that, both compound **7** and **16** exhibits the smectic A mesophase. The smectic mesophase length and smectic thermal stability of compound **16** is higher by 88°C and 83°C, respectively, than compound **7**. This is because of the greater molecular length of compound **16** provided by the additional aromatic ring and central ester linkage. As a result of its enhanced anisotropy of polarizability and increase in the intermolecular cohesive forces that are responsible for the wider mesophase length and higher thermal stability of smectic mesophase. This is also observed during comparison of compound **A** with compound **D**, and compound **B** with compound **E**. The mesophase length and thermal stability of compound **D** are higher by 57°C and 92°C, respectively, than that of compound **A**. Compound **D** also exhibits the nematic mesophase, due to the enhanced polarizability and increase in intermolecular cohesive forces, which are also responsible for this induction of the nematic mesophase. The nematic mesophase range and nematic thermal stability of compound **E** are higher by 101°C and 121°C, respectively, than compound **B**.

Reference to Table 5 shows that the smectic mesophase range and smectic phase thermal stability of compound **16** are higher by 103°C and 165°C than compound **F**. The absence of the nematic mesophase for compound **16** may be because of the polar -NO_2 group, which diminishes the nematic mesophase. Overall, compound **16** has greater mesophase thermal stability. By reference to the molecular structure of both compounds, it can be observed that both compounds have a fused ring system at the terminus of the molecule, but the compound **16** has 6-nitrobenzothiazole ring at the terminus which increases the overall polarizability of the molecule [25]. Although the compound **16** has a lateral nitro substituent, the effect pronounced by lateral substituent is eliminated by the presence of heterocyclic benzothiazole ring. In addition to this, the polar nature of lateral nitro group present in compound **16** also increases the polarizability of the molecule this, also assists to increase the thermal stability of the compound. This is also reflected in the comparison of compound **D** and compound **E** with compound **F**. Table 5 indicates that the smectic mesophase length and thermal stability of compound **D** is higher by 126°C and 152°C, respectively, than compound **F**, and the nematic mesophase length and thermal stability of compound **E** are higher by 55°C and 53°C, respectively, than compound **F**.

CONCLUSION

Two new mesogenic homologous series containing 6-nitrobenzothiazole moiety at the terminus of the molecule were synthesized. The mesomorphic properties exhibited by the present series I and II show that the members of series II exhibit higher mesophase thermal stability as compared to those of series I due to the presence of an additional phenyl ring and a central ester linkage. All the derivatives of both the present mesogenic homologous series exhibit higher mesophase thermal stabilities as compared to the naphthalene analogue having no lateral substituent. It was also observed that the nitro substituent is more conducive to the generation of smectic mesophase as compared to the chloro and the methoxy substituent.

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