

Mesogenic benzothiazole derivatives with methoxy substituents[†]

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Abstract. Two new mesogenic homologous series containing 6-methoxybenzothiazole ring at the terminus of the molecule, viz. 2-(4'-*n*-alkoxyphenylazo)-6-methoxybenzothiazoles and 2-[4'-(4''-*n*-alkoxybenzoyloxy)phenylazo]-6-methoxybenzothiazoles were synthesized. In series I, *n*-butyloxy to *n*-tetradecyloxy derivatives exhibit nematic mesophase. Smectic A mesophase commences from the *n*-dodecyloxy derivative as a monotropic phase and is retained up to the last member synthesized. All the members of series II exhibit enantiotropic nematic mesophase. The mesomorphic properties of the present series are compared with other structurally related series to evaluate the effect of the benzothiazole ring and the methoxy substituent on mesomorphism.

Keywords. 6-Methoxybenzothiazole; azomesogens; smectic A; nematic.

1. Introduction

The effects of different substituents and their position on mesogenic properties were widely studied by many researchers and the relation between them has been established.^{1–3}

Liquid crystals containing heterocyclic moieties have received great attention because of their interesting properties.⁴ The inclusion of a heteroatom can cause large changes in the kind of mesophase present or in the physical properties of the mesophase. Many mesogenic compounds containing heterocyclic rings have been reported in the literature. Single ring heterocyclic moieties such as pyridine,^{5–7} furyl,⁵ substituted pyrimidine carboxylic acid,⁸ thiazole,⁹ thiadiazole^{10–13} and oxadiazole¹² are reported in the literature. Barbera *et al*¹⁴ 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 reported¹⁵ in the literature. However, fused ring heterocyclic derivatives which are two condensed rings are practically planar and rigid molecules. Liquid crystals containing fused heterocyclic ring systems such as coumarin¹⁶ derivatives containing

azo central linkages, thiazole[5,4-*d*]thiazoles,¹⁷ imidazo[2,1-*b*]-1,3,4-thiadiazoles¹⁸ derivatives, isocoumarin¹⁹ derivatives having central ester and amide linkages exhibiting smectic C and nematic mesophase with very high mesophase transition temperatures, esters of 7-decanoyl oxychromone-3-carboxylic acid,^{20,21} flavone²² etc. are reported in the literature. Recently Xuelong *et al*²³ synthesized and studied the mesogenic properties of benzo-2,1-3-thiadiazole derivatives.

Pavluchenko *et al*²⁴ reported mesogens containing benzothiazole and benzoxazole with central linkages and lateral substitution at different positions so as to evaluate the effect of structural changes on mesomorphic properties. They observed that substitution at the sixth position was thermally more stable as compared to that at the fifth position on the benzothiazole ring. They also concluded that 6-substituted benzothiazoles in comparison with their benzoxazole analogs have higher mesophase transition temperatures because of the difference in degree of aromatization of azole cycles, viz. degree of conjugation of heteroatom *p*-electrons with *p*-electrons of cycle. Recently, we reported³² two mesogenic homologous series containing 6-chlorobenzothiazole ring systems with azo and/or ester central linkage. In order to study more about the effect of benzothiazole ring and methoxy substituent on mesomorphic properties in such systems, we have synthesized two new ex-

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tensive mesogenic homologous series of benzothiazole derivatives containing 6-methoxy substituents.

2. Experimental

2.1 Characterization

The structures of the compounds were confirmed by FTIR spectroscopy via KBr pellet, using a Shimadzu IR-408 spectrophotometer. ^1H 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. CDCl_3 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 $5^\circ\text{C}/\text{min}$. 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.

2.2 Materials

4-Hydroxybenzoic acid, 4-methoxybenzoic acid, 1-bromoalkanes, thionyl chloride, anhydrous potassium carbonate, sodium nitrite, 4-methoxyaniline, 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.

2.3 Synthesis

The synthetic route to series I and II is illustrated in schemes 1a and 1b respectively.

2.3a *2-Amino-6-methoxybenzothiazole* [2] was prepared from 4-methoxyaniline [1] by the reported method.²⁵ Crystallization from 1 : 1 aqueous ethanol afforded pure yellow needles of [2]. Yield: 64%. M.P. 165°C (reported²⁴ m.p.: $165\text{--}167^\circ\text{C}$).

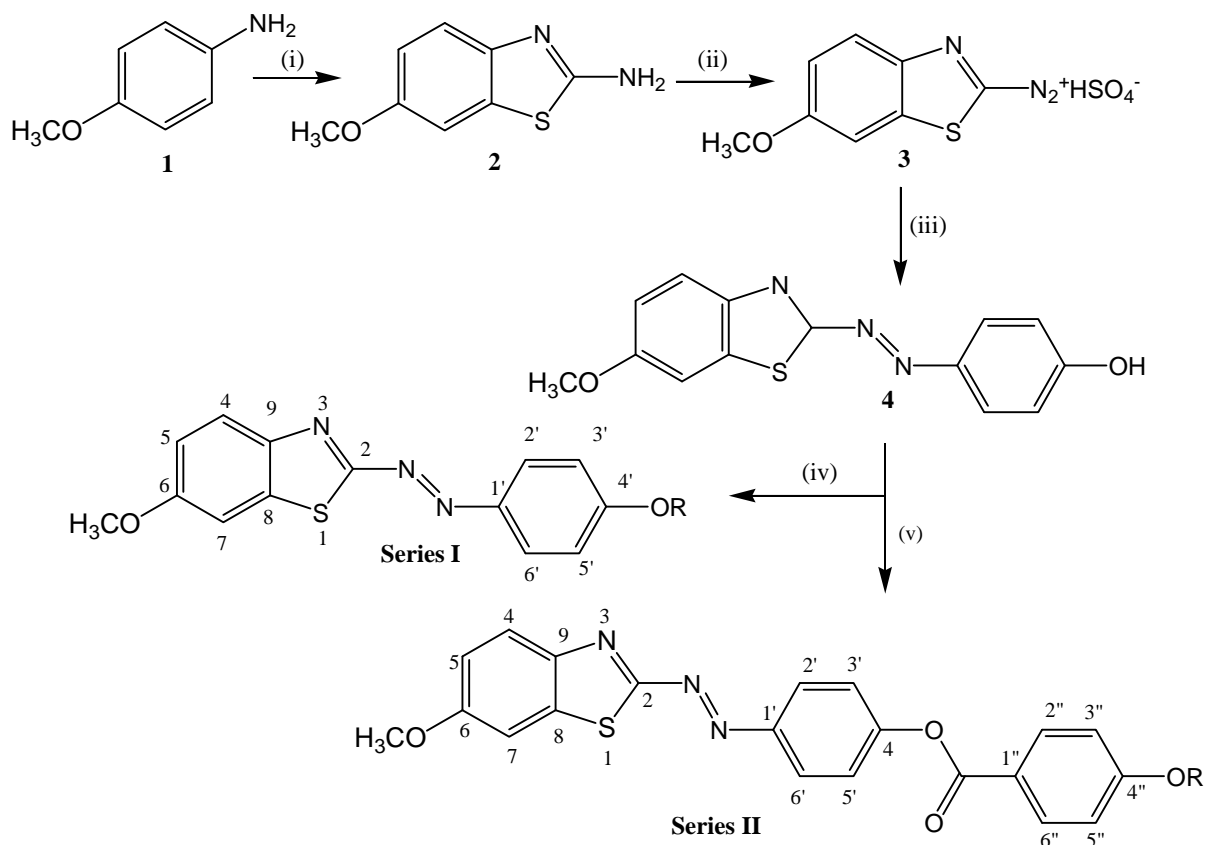
2.3b *2-(4-Hydroxyphenylazo)-6-methoxybenzothiazole* [4]: This was synthesized by diazotization of compound [2] and coupling with phenol by follow-

ing the method reported by Johari and Varshney.²⁶ The dye thus obtained was crystallized several times using alcohol till constant melting point was obtained. Yield: 58%, m.p.: 256°C . Elemental analysis: found C 58.46, H 3.51, N 14.98%, $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$ requires C 58.93, H 3.89, N 14.73%. The FTIR spectrum showed a broad peak of intermolecularly hydrogen bonded, phenolic $-\text{OH}$ at $3200\text{--}3600\text{ cm}^{-1}$. Other signals observed were at 3051 ($\nu_{\text{C-H}}$, aromatic), 2924 ($\nu_{\text{C-H}}$, aliphatic), 2360, 1600, 1495, 1267 (Ar-O-CH₃), 1057 (benzothiazole), 1015, 826, 690, 650 (C-S-C) cm^{-1} .

2.3c *2-(4-n-Alkoxyphenylazo)-6-methoxybenzothiazoles* [I]: These were synthesized by alkylation of dye [4] using the reported method of Vyas and Shah.²⁷ 2-(4'-Hydroxyphenylazo)-6-methoxybenzothiazole (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 TLC (10% ethylacetate: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: 54–63%. The elemental analysis of all the compounds of series I was satisfactory and results are listed in table 1. IR and ^1H NMR spectral data of *n*-decyloxy and *n*-tetradecyloxy derivatives as representative members are given below.

2-(4'-n-Decyloxyphenylazo)-6-methoxybenzothiazole – IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3041 ($\nu_{\text{C-H}}$, aromatic), 2922 ($\nu_{\text{C-H}}$, aliphatic), 2852, 2370, 1599 ($-\text{N}=\text{N}-$), 1489, 1464, 1263 (Ar-O-R), 1056 (benzothiazole), 832, 725, 694, 647 (C-S-C).

^1H NMR spectrum (CDCl_3 , 200 MHz): δ 8.00–8.04 (*m*, 3H, ArH at C-2' and C-6' and C-4) 7.30 (*d*, $J_{7,5} = 2.3\text{ Hz}$, 1H, ArH at C-7), 7.12 (*dd*, $J_{5,7} = 2.3\text{ Hz}$, $J_{5,4} = 8.8\text{ Hz}$, 1H, ArH at C-5), 7.02 (*d*, $J = 9\text{ Hz}$, 2H, ArH at C-3' and C-5'), 4.07 (*t*, 2H, Ar-O-CH₂-), 3.91 (*s*, 3H, Ar-O-CH₃), 1.82 (*m*, 2H, Ar-O-C-CH₂-), 1.28–1.58 (*m*, 14H, 7x-CH₂-), 0.87 (*t*, 3H, $-\text{CH}_3$).



(i) KSCN, Br₂, AcOH; (ii) NaNO₂, H₂SO₄, 0–5°C; (iii) phenol, 10% NaOH (aq.), 0–10°C; (iv) RBr, K₂CO₃, acetone; *Series I*: R=C_nH_{2n+1}, n = 4–8, 10, 12 and 16; (v) 4-*n*-alkoxybenzoyl chloride, pyridine; *Series II*: R=C_nH_{2n+1}, n = 1–8, 10, 12, 14 and 16.

Scheme 1. Synthetic route to series I and II.

2-(4'-*n*-Tetradecyloxyphenylazo)-6-methoxybenzothiazole – IR spectrum (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3049 ($\nu_{\text{C-H}}$, aromatic), 2930 ($\nu_{\text{C-H}}$, aliphatic), 2854, 2369, 1600 (–N=N–), 1493, 1467, 1262 (Ar-O-R), 1058 (benzothiazole), 832, 725, 694, 645 (C-S-C).

¹H NMR spectrum (CDCl₃, 200 MHz): **d** 8.00–8.03 (*m*, 3H, ArH at C-2' and C-6' and C-4) 7.30 (*d*, $J_{7,5} = 2.4$ Hz, 1H, ArH at C-7), 7.11 (*dd*, $J_{5,7} = 2.4$ Hz, $J_{5,4} = 8.7$ Hz, 1H, ArH at C-5), 7.01 (*d*, $J = 9$ Hz, 2H, ArH at C-3' and C-5'), 4.06 (*t*, 2H, Ar-O-CH₂-), 3.91 (*s*, 3H, Ar-O-CH₃), 1.82 (*m*, 2H, Ar-O-C-CH₂-), 1.26–1.61 (*m*, 22H, 11x-CH₂-), 0.88 (*t*, 3H, –CH₃).

2.3d 4-*n*-Alkoxybenzoic acids and 4-*n*-alkoxybenzoyl chlorides: These were synthesized by the modified method of Dave and Vora.²⁸

2.3e 2-[4ϕ(4²-*n*-Alkoxybenzoyloxy) phenylazo]-6-methoxybenzothiazoles [**II**]: The compound [4]

(0.02 mol) was dissolved in dry pyridine (5 ml) and a cold solution of 4-*n*-alkoxybenzoyl chloride (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 recrystallized several times from acetic acid till constant transition temperatures were obtained. Yield 62–70%. The elemental analysis of all compounds of series II was satisfactory and results are listed in table 1. IR and ¹H NMR spectral data of *n*-decyloxy and *n*-tetradecyloxy derivatives as representative members are given below.

2-[4ϕ(4²-*n*-Decyloxybenzoyloxy) phenylazo]-6-methoxybenzothiazole: IR spectrum (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3077 ($\nu_{\text{C-H}}$, aromatic), 2918 ($\nu_{\text{C-H}}$, aliphatic), 2849,

Table 1. Elemental analysis for series I and II.

Compound	R=C _n H _{2n+1} n =	Formula	% Required (% found)		
			C	H	N
<i>Series I</i>					
1	4	C ₁₈ H ₁₉ N ₃ O ₂ S	63.32(63.16)	05.61(5.85)	12.31(12.58)
2	5	C ₁₉ H ₂₁ N ₃ O ₂ S	64.20(64.45)	05.95(6.18)	11.82(11.53)
3	6	C ₂₀ H ₂₃ N ₃ O ₂ S	65.01(64.76)	06.27(6.04)	11.37(11.08)
4	7	C ₂₁ H ₂₅ N ₃ O ₂ S	65.77(65.32)	06.57(6.77)	10.96(11.27)
5	8	C ₂₂ H ₂₇ N ₃ O ₂ S	66.47(66.33)	06.85(7.04)	10.57(10.19)
6	10	C ₂₄ H ₃₁ N ₃ O ₂ S	67.73(67.61)	07.34(7.51)	09.87(09.53)
7	12	C ₂₆ H ₃₅ N ₃ O ₂ S	68.84(68.72)	07.78(7.49)	09.26(09.02)
8	14	C ₂₈ H ₃₉ N ₃ O ₂ S	69.82(69.71)	08.16(8.37)	08.72(09.06)
9	16	C ₃₀ H ₄₃ N ₃ O ₂ S	70.69(70.91)	08.50(8.13)	08.24(07.83)
<i>Series II</i>					
1	1	C ₂₂ H ₁₇ N ₃ O ₄ S	63.00(63.37)	4.09(4.31)	10.02(9.72)
2	2	C ₂₃ H ₁₉ N ₃ O ₄ S	63.73(63.42)	4.42(4.25)	9.69(9.57)
3	3	C ₂₄ H ₂₁ N ₃ O ₄ S	64.41(64.70)	4.73(4.57)	9.39(9.83)
4	4	C ₂₅ H ₂₃ N ₃ O ₄ S	65.06(65.38)	5.02(5.44)	9.10(9.35)
5	5	C ₂₆ H ₂₅ N ₃ O ₄ S	65.65(65.26)	5.30(5.73)	8.84(8.43)
6	6	C ₂₇ H ₂₇ N ₃ O ₄ S	66.24(66.73)	5.56(5.20)	8.58(8.21)
7	7	C ₂₈ H ₂₉ N ₃ O ₄ S	66.78(66.31)	5.80(5.98)	8.34(8.66)
8	8	C ₂₉ H ₃₁ N ₃ O ₄ S	67.29(67.75)	6.04(5.71)	8.12(8.53)
9	10	C ₃₁ H ₃₅ N ₃ O ₄ S	68.23(67.84)	6.46(6.74)	7.70(8.04)
10	12	C ₃₃ H ₃₉ N ₃ O ₄ S	69.08(68.63)	6.85(7.23)	7.32(6.87)
11	14	C ₃₅ H ₄₃ N ₃ O ₄ S	69.85(70.29)	7.20(6.93)	6.98(7.18)
12	16	C ₃₇ H ₄₇ N ₃ O ₄ S	70.56(70.79)	7.52(7.85)	6.67(6.40)

1719 (–COO–), 1605 (–N=N–), 1554, 1492, 1432, 1261 (Ar-O-CH₃), 1057 (benzothiazole), 845, 653 (C-S-C).

¹H NMR spectrum (CDCl₃, 300 MHz): **d** 8.04–8.18 (*m*, 5H, ArH at C-2'', C-6'', C-2', C-6' and C-4), 7.45 (*d*, *J* = 8.8 Hz, 2H, ArH at C-3' and C-5'), 7.33 (*d*, *J*_{7,5} = 2.3 Hz, 1H, ArH at C-7), 7.13 (*dd*, *J*_{5,7} = 2.3 Hz, *J*_{5,4} = 9 Hz, 1H, ArH at C-5), 7.00 (*d*, *J* = 9 Hz, 2H, ArH at C-3'' and C-5''), 4.06 (*t*, 2H, Ar-O-CH₂–), 3.92 (*s*, 3H, Ar-O-CH₃), 1.83 (*m*, 2H, Ar-O-C-CH₂–), 1.28–1.58 (*m*, 14H, 7x-CH₂–), 0.89 (*t*, 3H, –CH₃).

2-[4*ϕ*(4²-*n*-Tetradecyloxybenzoyloxy) phenylazo]-6-methoxybenzothiazole: IR spectrum (KBr) **n**_{max}/cm^{–1}: 3078 (**n**_{C-H}, aromatic), 2919 (**n**_{C-H}, aliphatic), 2850, 1731 (–COO–), 1606 (–N=N), 1555, 1492, 1435, 1262 (Ar-O-CH₃), 1062 (benzothiazole), 843, 650 (C-S-C).

¹H NMR spectrum (CDCl₃, 300 MHz): **d** 8.05–8.17 (*m*, 5H, ArH at C-2'', C-6'', C-2', C-6' and C-4), 7.43 (*d*, *J* = 8.7 Hz, 2H, ArH at C-3' and C-5'), 7.33 (*d*, *J*_{7,5} = 2.1 Hz, 1H, ArH at C-7), 7.13 (*dd*, *J*_{5,7} = 2.1 Hz, *J*_{5,4} = 8.7 Hz, 1H, ArH at C-5), 6.93–7.0 (*m*, 2H,

ArH at C-3'' and C-5''), 3.84–4.08 (*m*, 5H, 2H of Ar-O-CH₂ and 3H of Ar-O-CH₃), 1.8–1.85 (*m*, 2H, Ar-O-C-CH₂–), 1.27–1.46 (*m*, 22H, 11x-CH₂–), 0.88 (*t*, 3H, CH₃).

3. Results and discussion

3.1 Microscopic observation and DSC for series I and II

The mesophase exhibited by series I and II compounds is identified by examining the thin film of a sample sandwiched between a glass slide and cover slip. In series I compounds, on cooling the isotropic liquid, small droplets appear which coalesce to marble/schlieren texture characteristic of the nematic phase. On further cooling, the higher members (*n* ≥ 12) show focal conic texture characteristic of SmA mesophase. In all the compounds of series II, on cooling the isotropic liquid, small droplets appeared which coalesce to classical schlieren (threaded) or marble textures characteristic of the nematic phase. Transition temperatures obtained for both the series are recorded in table 2 (enantiotropic phase temperatures are recorded in heating cycle).

Table 2. Transition temperatures (°C) of the series I and II compounds.

Compound	R=-C _n H _{2n+1}	n =	Cr	SmA	N	I
<i>Series I</i>						
1	4		• 102	–	• 141	•
2	5		• 106	–	• 140	•
3	6		• 112	–	• 138	•
4	7		• 87	–	• 137	•
5	8		• 94	–	• 136	•
6	10		• 98	–	• 135	•
7	12		• 113	• (0·108)*	• 135	•
8	14		• 105	• (0·100)	• 132	•
9	16		• 102	• (0·99)	• 118	•
<i>Series II</i>						
10	1		• 158	–	• 296	•
11	2		• 162	–	• 295	•
12	3		• 152	–	• 291	•
13	4		• 155	–	• 282	•
14	5		• 134	–	• 273	•
15	6		• 131	–	• 269	•
16	7		• 128	–	• 267	•
17	8		• 126	–	• 265	•
18	10		• 130	–	• 261	•
19	12		• 131	–	• 254	•
20	14		• 135	–	• 244	•
21	16		• 129	–	• 238	•

()*Monotropic value; Cr: crystalline solid phase; Sm A: smectic A phase; N: nematic Phase; I: isotropic liquid phase; •: phase exists; –: phase does not exist

Table 3. DSC data for series I and II compounds.

Series	Compound	Transition	Peak temp. (°C)	ΔH (J g ⁻¹)	ΔS (Jg ⁻¹ K ⁻¹)	
I	6	Cr-N	100·5	57·5	0·1539	
		N-I	132·9	1·6	0·039	
	8	(Heating cycle)				
		Cr-N	105·5	59·91	0·1583	
		N-I	130·1	1·73	0·0043	
		(Cooling cycle)				
I-N	129·5	1·53	0·0054			
N-SmA	099·3	2·19	0·1309			
SmA-Cr	093·5	48·72	0·0042			
II	18	Cr-N	130·1	75·43	0·1871	
		N-I	260·2	1·71	0·0032	
	20	Cr-N	137·6	90·1	0·2143	
		N-I	245·0	1·90	0·0037	

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 two compounds of

each series i.e. series I and II were measured by differential scanning calorimetry. Data are recorded in table 3. Enthalpy values of the phase transitions agree well with the existing literature value²⁹ which has helped in further confirmation of the mesophase type.

3.2 The phase behaviour of series I and II

3.2a Series I – 2-(4-*n*-Alkoxyphenylazo)-6-methoxybenzothiazoles: Nine homologues have been synthesized. *n*-Butyloxy to *n*-decyloxy derivatives exhibit an enantiotropic nematic mesophase. *n*-Dodecyloxy to *n*-hexadecyloxy derivatives exhibit polymorphism, as these members shows nematic and monotropic smectic A mesophases. The transition temperatures are recorded in table 2. It is clear from the plot of transition temperatures against the number of carbon atom in the alkoxy chain (figure 1) that the *N-I* transition shows falling tendency with increase in the chain length. SmA-*N* transition shows steep falling tendency as the series ascended.

3.2b Series II – 2-[4-(4²-*n*-Alkoxybenzoyloxy)phenylazo]-6-methoxybenzothiazoles: All the twelve members synthesized exhibit enantiotropic nematic mesophases. The transition temperatures are recorded in table 2. It can be noticed from the plot of

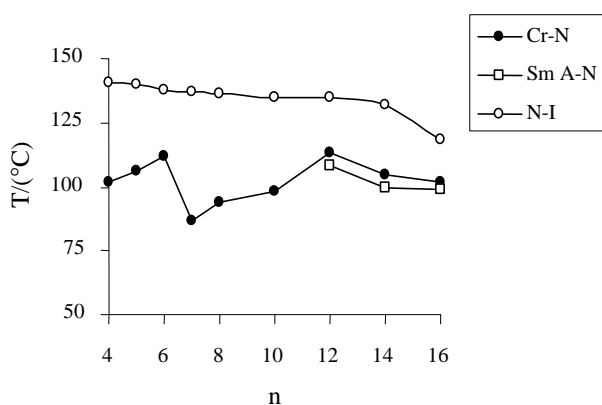


Figure 1. The phase behaviour of series I.

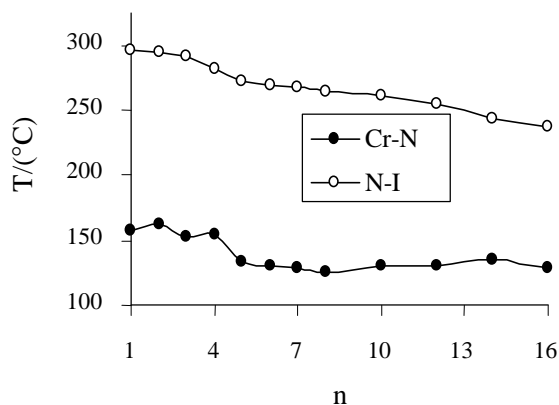


Figure 2. The phase behaviour of series II.

transition temperatures against the number of carbon atoms in the alkoxy chain (figure 2) that *N-I* transition temperatures exhibit a falling tendency with increase in terminal alkoxy tail. This is in agreement with the observation reported for such homologous series.³⁰

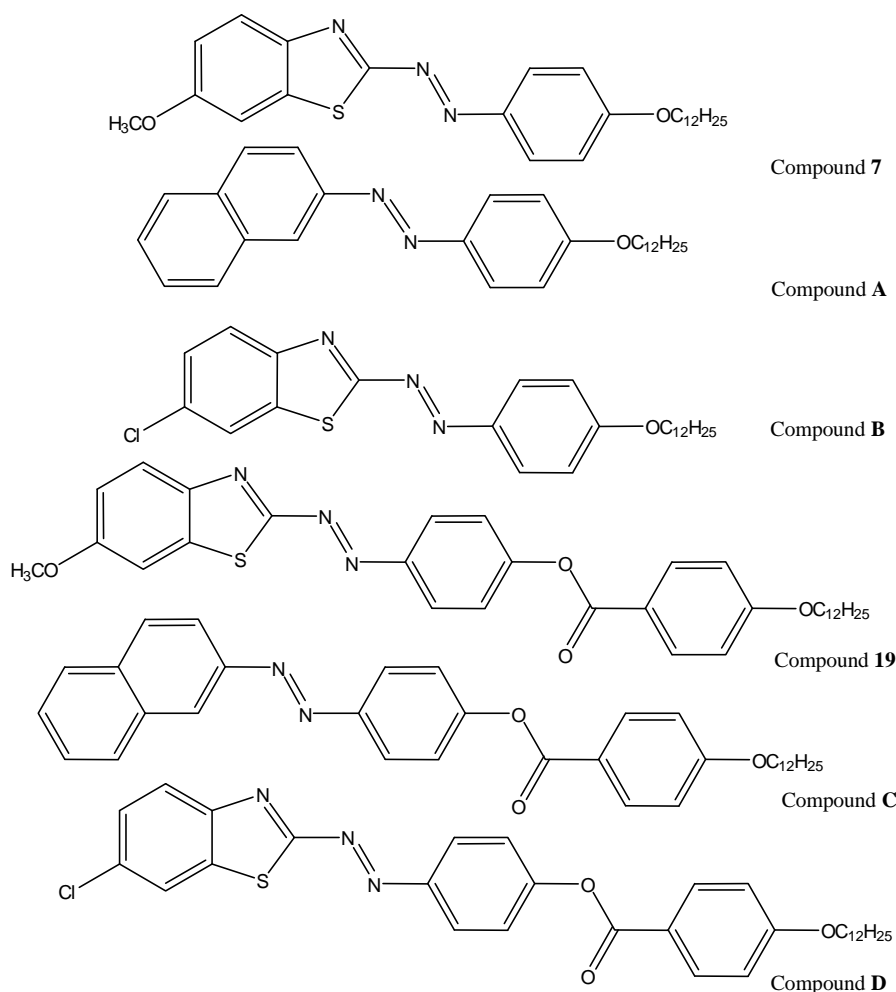
3.3 Mesogenic properties and molecular constitution

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.

Table 4 shows the comparison of transition temperatures, range (width) of mesophase phase and thermal stabilities and molecular structures of representative compounds **7** (*n* = 12) and **19** (*n* = 12) of the present series I and II with other structurally related compounds **A**³¹, **B**³², **C**³¹ and **D**³² reported in the literature. Both compounds **7** and **19** exhibit enantiotropic nematic mesophases. Mesophasic length and nematic thermal stability of compound **19** are higher by 101°C and 119°C respectively than that of **7**. This is because of the greater length of compound **19** provided by the additional aromatic ring and ester linkage.

Table 4 shows that compound **A** is non-mesogenic, whereas compound **7** is mesogenic and exhibits enantiotropic nematic and monotropic SmA mesophases. Reference to molecular structure shows that compound **A** differs only at one terminus. Compound **7** has a 6-methoxy benzothiazole ring at the terminus instead of the naphthalene ring of compound **A**. Presence of the terminal benzothiazole ring increases the overall polarizability of the molecule while lowering the symmetry of the molecule as compared to phenyl/naphthyl derivatives and provides higher transition temperature.²⁴

Table 4 further shows that compound **19** is purely nematogenic. Nematic mesophase length and nematic phase thermal stability of compound **19** are higher by 55°C and 53°C respectively than that of compound **C**. Both the compounds differ only at one terminus. The absence of smectic mesophase in compound **19** may be due to the methoxy substituent, which diminishes the smectic mesophase. However, the higher mesophase thermal stability of compound **19** compared to compound **C** may be because of the terminal benzothiazole ring system.²⁴

Table 4. The transition temperatures (°C), the mesophase range and molecular structure of compounds **7**, **19**, **A**, **B**, **C** and **D**.

Compound	Transition temperatures (°C)					Mesophase length		Commencement of smectic phase
	Cr	Sm	N	I	N	Sm		
7	• 113	–	(108)*	• 135	• 22	7	C ₁₂	
A	• –	–	–	• 94	• –	–	–	
B	• 80	• –	–	• 172	• –	92	C ₅	
19	• 131	–	• 254	• 123	• –	–	–	
C	• (112)	• 133	• 201	• 68	• 23	C ₈		
D	• 115	• 264	• 268	• 4	• 149	C ₁		

(*)Monotropic value

Table 4 also shows that the compound **7** exhibit enantiotropic nematic mesophase along with monotropic SmA mesophase, whereas compound **B** exhibits enantiotropic SmA mesophase. The smectic mesophase length and smectic thermal stability of compound **B** is higher by 85°C and 64°C respectively

than compound **7**. These may be because of the presence of the more polar –Cl group at the sixth position in compound **B** as compared to the less polar –OCH₃ group at the same position in compound **7**. The more polar –Cl group increases the molecular polarizability and possibly also the molecular dipole

larity of compound **B** compared to compound **7**. This is also seen in the comparison between compound **19** with compound **D**.

4. Conclusions

Liquid crystalline properties depend on the molecular structure. However, if a specific type of liquid crystal phase is required to exist over a particular range of temperature, then molecular structure should be carefully designed. To obtain compound, showing the nematic mesophase with good mesophase lengths and higher phase transitions, we have synthesized two new mesogenic homologous series with 6-methoxybenzothiazole ring at the terminus. Compounds of series I exhibit low temperature nematic mesophases as compared to those of series II, except that the last three members of series I exhibit smectic mesophase, whereas series II is purely nematogenic.

By comparing the present series with other structurally related series it is found that the benzothiazole ring effects greatly the mesophase thermal stability. The study also shows that a methoxy substituent positions of the benzothiazole ring favours the formation of the nematic mesophase.

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