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J. Belmar

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New liquid crystals containing the benzothiazol unit: amides and azo compounds

J. BELMAR, M. PARRA, C. ZÚÑIGA*, C. PÉREZ, C. MUÑOZ
Facultad de Ciencias Químicas, Departamento de Química Orgánica,
Universidad de Concepción, Casilla 3-C, Concepción, Chile

A. OMENAT and J. L. SERRANO
Química Orgánica, Facultad de Ciencias-ICMA, Universidad de Zaragoza-CSIC,
50009-Zaragoza, Spain

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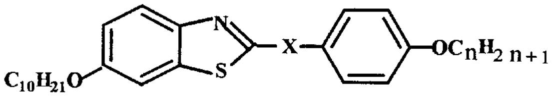
Two series of calamitic liquid crystals containing a benzothiazole ring within the central core and two different linkage groups (amide and azo) have been prepared and their liquid crystalline properties studied and compared with those of the analogous series of imines. The influence of the linkage group within the central core has been proven to determine the variety of mesomorphism displayed by the compounds. The compounds with imine and azo linkages behave in a similar way and exhibit typical nematic and smectic C mesophases. Compounds incorporating an amide linkage show a poorer mesomorphism and mainly present a smectic C mesophase.

1. Introduction

The introduction of heterocycles within the central core of a classical calamitic molecule has been found to be an interesting strategy to follow for the design of new liquid crystalline materials because of great possibilities in the variation of direction and magnitude of their permanent dipole moments and, in consequence, variations of their mesomorphism and potential electro-optical properties.

Many different heterocyclic liquid crystalline compounds have been synthesized and their properties reported in the literature. The heterocycles involved are usually 5- or 6-membered and they form part of the central core in a typical rod-shape molecule. In 1976, a family of benzothiazole-derived members showed nematic mesomorphism but a systematic study of their properties was not described. In addition, some compounds containing the benzoxazole and benzothiazole rings have been studied as they exhibit interesting photophysical and fluorescent properties [2, 3].

For these reasons, and as part of our current work on the study of new heterocyclic derivatives showing liquid crystalline properties, we have synthesized three series of benzothiazole derivatives showing a typical rod-like geometry and incorporating three different linkage groups within the central core: imine-derivatives [4] (Series I), amide-derivatives (Series II) and Azo-derivatives (Series III). The general structure for the compounds in the three series is given in the following structure. The present work describes the synthesis, mesomorphic properties and a comparative study of the influence of the linkage group on the mesomorphism of the materials.



SERIES I X = N=CH (IMINE)

SERIES II X = NHCO (AMIDE)

SERIES III X = N≡N (AZO)

2. Synthesis

Amides (**4**) and azocompounds (**5**) were synthesized according to the general procedure outlined in the scheme. 2-Amino-6-*n*-decyloxybenzothiazole (**2**) was obtained following the procedure described in [4], involving the condensation of 4-*n*-decyloxyaniline with potassium thiocyanate. The arylthiourea thus obtained is then cyclized with bromine. Attempted cyclization

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*Author for correspondence.

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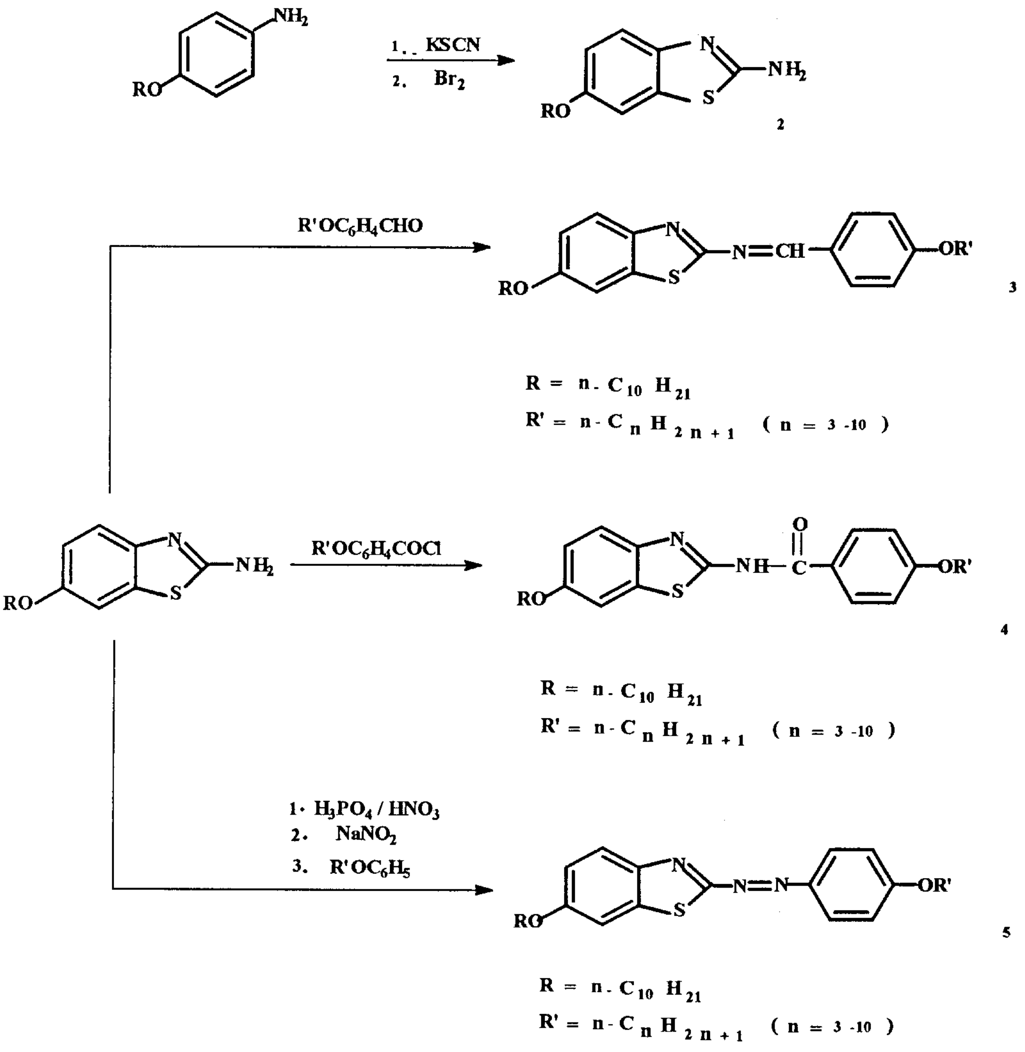


Scheme.

with SO_2Cl_2, as used previously in the synthesis of 2-amino-6-methylbenzothiazole [5], was unsuccessful in the present work.

The azo compounds were obtained by the reaction of alkoxybenzenes with the diazonium salt of 6-*n*-decyloxy-2-aminobenzothiazole. Sodium nitrite was used in a H_3PO_4/HNO_3 medium, as described for the diazotation of 2-amino-4-methoxylbenzothiazole [6].

3. Results and discussion

The thermal, thermodynamical and mesomorphic properties of compounds of series I, II, and III are gathered in tables 1, 2, and 3, respectively. A graphical representation of the mesomorphic behaviour as a function of the number (*n*) of carbon atoms in the lateral chain for the three series is given in figures 1, 2 and 3, respectively.

The assignment of the mesophase type was made on the basis of the textures observed by polarizing optical microscopy as all of the mesophases display the typical textures for nematic (N) and smectic C (SmC) phases [7].

Compounds in series I and III show a very similar mesomorphic behaviour (in terms of transition temperatures and mesophase type), displaying nematic and smectic C mesomorphism. The nematic mesophase is present in the whole range of *n* studied. This fact indicates that similar molecular interactions take place, giving rise to the same type of molecular arrangement and thermal stability. This is not difficult to understand taking into account the structure and geometry of the molecules involved in these series (figure 4). The members in both series with short alkyloxy chains (*n* = 3–6) show a nematic mesophase; a lateral interaction to give rise

Table 1. Transition temperatures and enthalpies for 6-*n*-decyloxy-2-(4-alkoxybenzylidenamino)benzothiazoles (**3**).

n	Transition	Temperature/°C	Δ*H*/kJ mol^{-1}
3	Cr_1–Cr_2	75.0	
	Cr_2–N	79.9	25.9
	N–I	103.2	0.5
4	Cr–N	85.0	40.7
	N–I	118.9	1.1
5	Cr–N	75.9	35.6
	N–I	112.2	1.2
6	Cr–SmC	82.7	39.4
	SmC–N	88.9	0.6
	N–I	121.1	1.4
7	Cr–SmC	80.8	36.7
	SmC–N	101.2	0.9
	N–I	120.3	1.8
8	Cr–SmC	82.6	40.1
	SmC–N	112.1	1.2
	N–I	123.0	2.5
9	Cr–SmC	80.8	38.3
	SmC–N	116.4	1.9
	N–I	121.7	2.9
10	Cr–SmC	81.3	40.0
	SmC–N	121.6	
	N–I	122.7	8.1

to a layered smectic order is not favoured because of the difference of the volume occupied by the flexible melted chains (one side is fixed in C_{10}), and only a short range positional order is achieved. As the length of both alkyloxy chains becomes similar (*n* = 7–10), the tilted smectic order is favoured.

Table 2. Transition temperatures and enthalpies for *N*-[2-(6-*n*-decyloxybenzothiazolyl)]-4-*n*-alkoxybenzamides (**4**).

n	Transition	Temperature/°C	Δ*H*/kJ mol^{-1}
3	Cr_1–Cr_2	72.4	
	Cr_2–Cr_3	100.6	8.4
	Cr_3–Cr_4	104.8	0.6
	Cr_4–I (broad)	112.6	10.5
4	Cr_1–Cr_2	119.3	24.7
	Cr_2–Cr_3	128.4	
	Cr_3–I	138.6	2.2
5	Cr_1–Cr_2	80.9	19.5
	Cr_2–I	134.8	25.2
6	Cr_1–Cr_2	104.7	21.2
	Cr_2–I	124.4	18.1
	I–N	121.0	1.2
7	Cr_1–Cr_2	83.9	13.2
	Cr_2–SmC	104.9	28.2
	SmC–I	137.4	4.9
8	Cr_1–Cr_2	88.0	
	Cr_2–SmC	100.5	32.1
	SmC–I	132.8	4.0
9	Cr_1–Cr_2	73.5	7.9
	Cr_2–Cr_3	86.2	2.8
	Cr_3–SmC	101.6	26.1
	SmC–I	135.1	4.6
10	Cr_1–Cr_2	100.6	24.4
	Cr_2–SmC	116.0	18.3
	SmC–N	124.5	0.8
	N–I	127.5	2.1

Compounds in series II show a different mesomorphic behaviour. In this case, no mesophase is observed for the members with a short terminal chain (*n* = 3–5). The

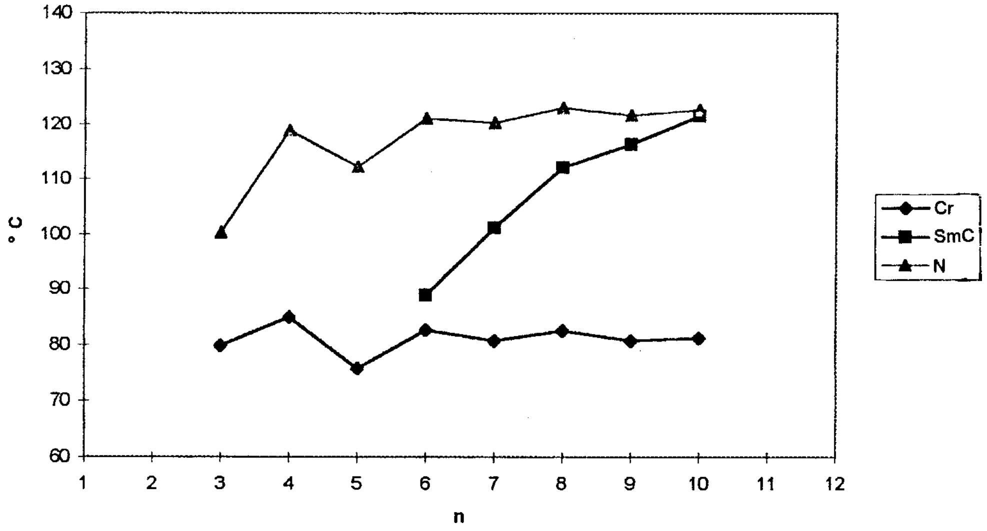


Figure 1. Mesomorphic behaviour as a function of the number of carbon atoms in the terminal alkoxy chain for compounds in series I.

compound with $n = 6$ shows a monotropic nematic mesophase which becomes enantiotropic for compounds with $n > 7$ onwards and they have a higher melting point compared with their homologues in series I and II. Compounds with $n = 7$–10 show a smectic C mesophase. This mesophase tends to disappear for $n > 10$, although this trend has not been proven experimentally. The mesomorphic behaviour of compounds in series II can be explained by taking into account the formation of H-bonding between molecules as shown in figure 5. This parallel molecular arrangement would encourage smectic mesomorphism by providing additional lateral intermolecular attraction and by lining up molecules in a layered order [8, 9].

Table 3. Transition temperatures and enthalpies for 6-*n*-decyloxy-2-(4-*n*-alkoxyphenylazo)benzothiazoles (**5**).

n	Transition	Temperature/°C	ΔH/kJ mol^{-1}
3	Cr–N	80.8	32.6
	N–I	112.7	0.7
4	Cr–N	83.8	50.7
	N–I	121.9	0.8
5	Cr–N	62.3	21.4
	N–I	115.4	0.8
6	Cr$_1$–Cr$_2$	65.4	6.8
	Cr$_2$–SmC	48.3	
	SmC–N	75.2	34.5
	N–I	121.7	1.1
7	Cr–SmC	74.4	47.0
	SmC–N	79.5	
	N–I	121.2	1.2
8	Cr–SmC	70.7	44.9
	SmC–N	95.0	0.8
	N–I	123.8	1.8
9	Cr–SmC	74.5	22.7
	SmC–N	116.2	0.9
	N–I	123.3	1.8
10	Cr$_1$–Cr$_2$	56.0	2.6
	Cr$_2$–SmC	77.9	21.5
	SmC–N	114.7	6.0
	N–I	123.1	

As we saw for the series I and III, the smectic order is not favoured for members with a short alkyloxy chain, and the same applies for series II. However, the existence of H-bonding between molecules prevents the formation of a nematic phase, as both a positional and an orientational order are established. When this molecular order is broken an isotropic phase is obtained. For compounds with $n = 7$–10, a layered smectic order is favoured which is fully compatible with a molecular arrangement resulting from the intermolecular H-bonding which develops in the tilt direction and thus stabilizes the tilt of the smectic phase [10].

The occurrence of a tilted smectic C mesophase in the members of all the series opens an interesting possibility for further studies with this type of compound, such as the introduction of a chiral terminal alkyl chain in the calamitic structure in order to obtain chiral mesophases (cholesteric, tilted smectic) which would exhibit interesting electro-optical properties. In addition, further studies on the fluorescence of these materials could provide interesting possibilities for technological applications.

4. Experimental

The purity of compounds synthesized was evaluated by thin layer chromatography and elemental analysis (table 4). The structures were confirmed by ^{1}H NMR,

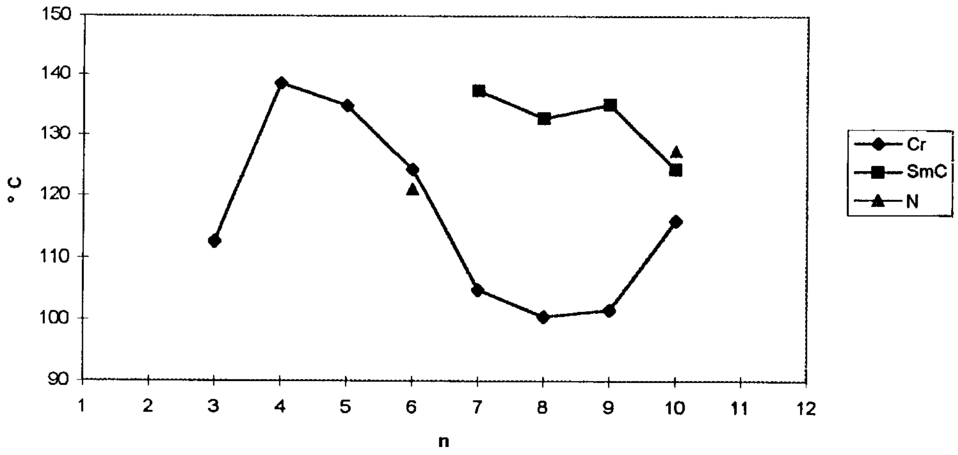


Figure 2. Mesomorphic behaviour as a function of the number of carbon atoms in the terminal alkoxy chain for compounds in series II.

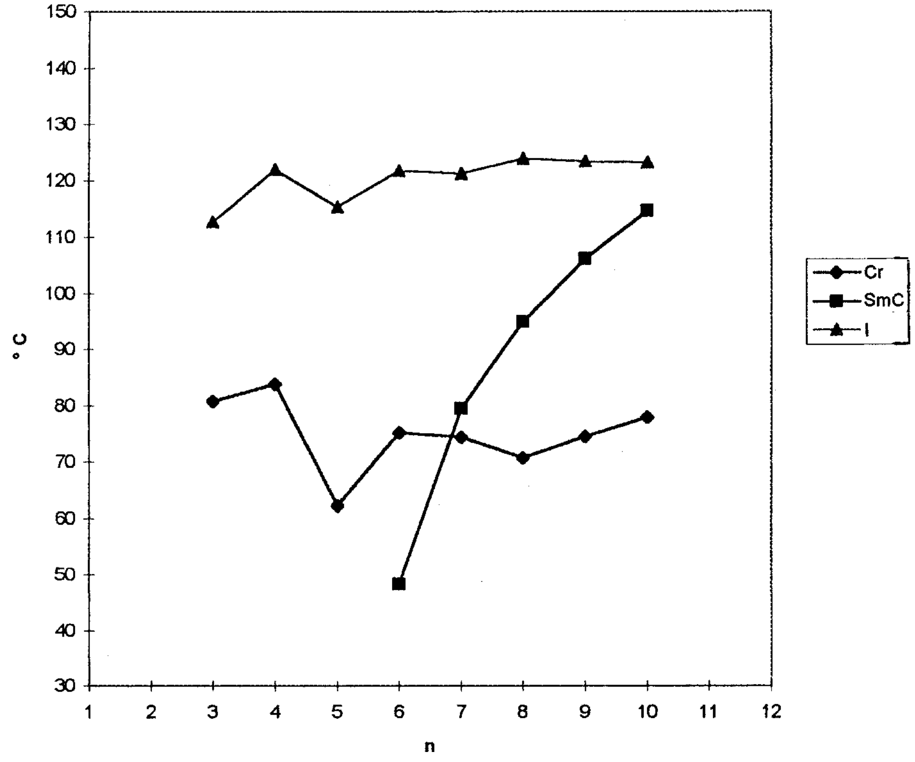


Figure 3. Mesomorphic behaviour as a function of the number of carbon atoms in the terminal alkoxy chain for compounds in series III.

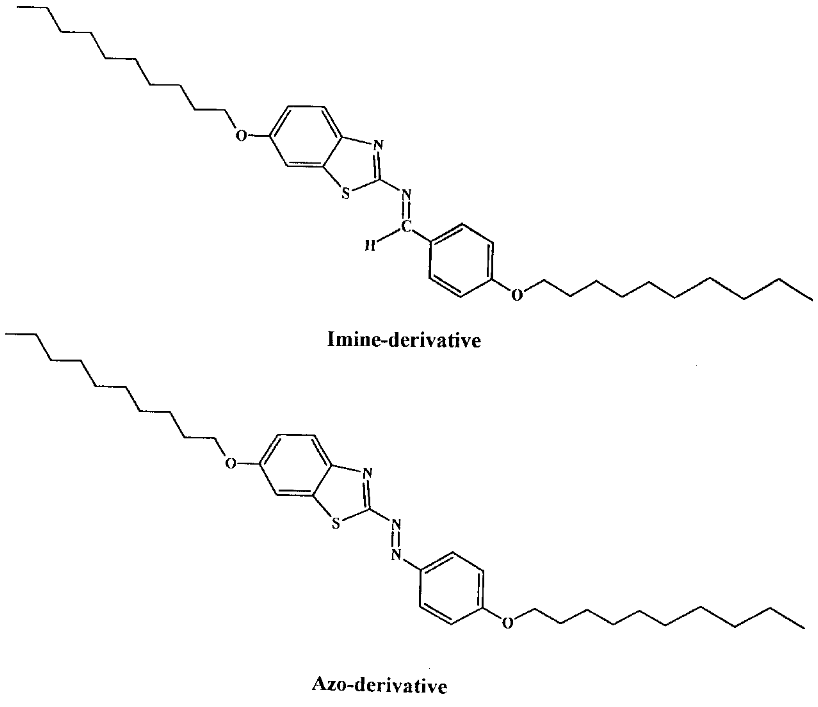


Figure 4. Structures for compounds in series I and III.

^{13}C NMR (Bruker AC-250P) and FTIR (Nicolet 550) spectra. Reported chemical shift values of benzothiazole, correlation spectra ^{1}H/^{13}C and DEPT spectra were used to assign the chemical shifts in ^{13}C spectra of the synthesized compounds. Table 5 contains spectroscopic data for the homologues with $n = 10$ of series II and III.

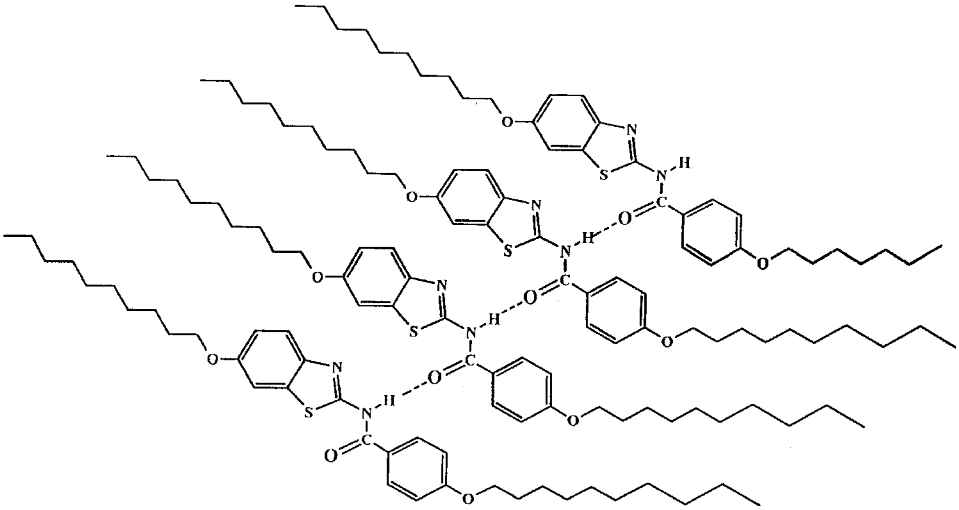


Figure 5. Structures for compounds in series II.

Table 4. Elemental analysis of *N*-[2-(6-*n*-decyloxybenzothiazolyl)]-4-alkoxybenzamides (series II) and 6-*n*-decyloxy-2-(4-*n*-alkoxyphenylazo)benzothiazoles (series III).

Empirical formula *R*: $-OC_nH_{2n+1}$	C/%		H/%		N/%	
	Calculated	Found	Calculated	Found	Calculated	Found
Amides						
$n = 3$ $C_{27}H_{36}N_2SO_3$	69.23	69.68	7.69	7.85	5.98	5.84
$n = 4$ $C_{28}H_{38}N_2SO_3$	69.70	70.01	7.88	8.09	5.81	5.64
$n = 5$ $C_{29}H_{40}N_2SO_3$	70.16	69.72	8.06	8.23	5.64	5.74
$n = 6$ $C_{30}H_{42}N_2SO_3$	70.59	70.57	8.23	8.54	5.49	5.50
$n = 7$ $C_{31}H_{44}N_2SO_3$	70.99	71.07	8.40	8.54	5.30	5.59
$n = 8$ $C_{32}H_{46}N_2SO_3$	71.37	71.52	8.55	8.69	5.20	5.34
$n = 9$ $C_{33}H_{48}N_2SO_3$	71.74	71.81	8.69	9.05	5.07	5.24
$n = 10$ $C_{34}H_{50}N_2SO_3$	72.08	72.43	8.83	9.95	4.95	5.34
Azo compounds						
$n = 3$ $C_{26}H_{35}N_3SO_2$	68.87	68.72	7.37	7.32	9.27	9.19
$n = 4$ $C_{27}H_{37}N_3SO_2$	69.38	69.32	7.92	7.61	8.99	8.97
$n = 5$ $C_{28}H_{39}N_3SO_2$	69.85	69.50	8.11	8.50	8.73	8.32
$n = 6$ $C_{29}H_{41}N_3SO_2$	70.30	70.06	8.28	8.07	8.48	8.53
$n = 7$ $C_{30}H_{43}N_3SO_2$	70.73	70.28	8.45	8.36	8.32	8.31
$n = 8$ $C_{31}H_{45}N_3SO_2$	70.94	71.24	8.60	8.33	8.03	7.78
$n = 9$ $C_{32}H_{47}N_3SO_2$	71.50	71.21	8.75	8.64	7.82	7.90
$n = 10$ $C_{33}H_{49}N_3SO_2$	71.87	71.26	8.89	8.85	7.62	7.69

4.1. *4-n-Decyloxyaniline*

This compound was synthesized according to [11].

4.2. *n-Alkyloxybenzenes*

These were synthesized by the conventional esterification of phenol.

4.3. *6-n-Decyloxy-2-aminobenzothiazole (**2**) and 6-n-decyloxy-2-(4-alkoxybenzylidenamino)-benzothiazoles (**3**)*

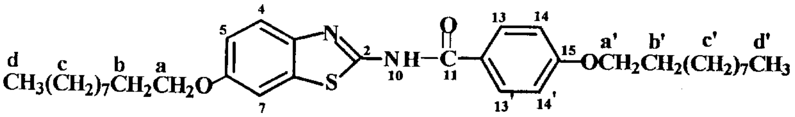
These compounds were prepared as described in [4].

4.4. *N-[2-(6-n-decyloxybenzothiazolyl)]-4-alkoxybenzamides (**4**)*

A mixture of 0.0033 mol of 4-*n*-alkoxybenzoic acid and 10 ml of thionyl chloride were heated under reflux for 2 h; the excess thionyl chloride was then removed under vacuum. 1 ml of triethylamine and 0.92 g (0.003 mol) of 6-*n*-decyloxy-2-aminobenzothiazole (**2**) in 10 ml of toluene were then added to the crude acyl chloride in 10 ml of toluene. The mixture was heated under reflux for 1 h and then poured onto water-ice mixture. The product was extracted with toluene and purified by

Table 5. Spectral data for compounds in series II and III.

*N-[2-(6-n-Decyloxybenzothiazolyl)]-4-n-decyloxybenzamides (**4**, n = 10)*



Chemical shifts of ^{1}H NMR (CDCl$_3$)

4	5	7	10	13–13′	14–14′	a + a′	b + b′	c + c′	d + d′
7.0 (d) J_{45} = 8.9	6.7 (d) J_{54} = 8.8	7.2 (d) J_{75} = 2.3	12 (s)	7.9 (d) J = 8.8	6.7 (d) J = 8.8	3.9 (m)	1.7 (m)	1.1–1.5 (m)	0.8 (m)

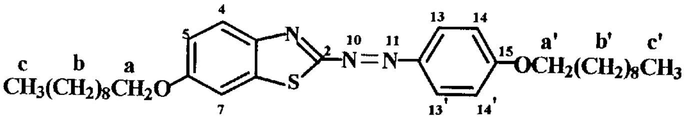
Chemical shifts of ^{13}C NMR (CDCl$_3$)

C–2	C–4	C–5	C–6	C–7	C–8	C–9	C-11	C–12	C–13–13′	C–14–14′	C–15
157.95	121.23	115.42	156.28	104.89	142.01[a]	133.10	165.21[a]	123.93	129.92	114.65	162.99

Alkoxy chains = 68.71, 68.33 (OCH$_2$); 31.87; 31.72; 29.55; 29.40; 29.30; 28.99; 26.05; 25.90; 22.64; 14.06.

IR (KBr)/cm^{-1} = 3077 (N–H); 1679 (C=O)

*6-n-Decyloxy-2-(4-n-decyloxyphenylazo)benzothiazoles (**5**, n = 10)*



Chemical shifts of ^{1}H RMN (CDCl$_3$)

4	5	7	11–11′	12–12′	a + a′	b + b′	c + c′
7.99 (d) J_{45} = 8.8	7.07 (d) J_{54} = 8.9 J_{57} = 2.3	7.25 (d) J_{75} = 2.3	7.99 (d) J = 8.8	6.98 (d) J = 8.9	1.7–1.9 (m)	1.2–1.6 (m)	0.9 (t)

Chemical shifts of ^{13}C NMR (CDCl$_3$)

C–2	C–4	C–5	C–6	C–7	C–8	C–9	C–12	C–13–13′	C–14–15′	C–15
173.89	125.39	116.52	158.9	105.06	131.50	146.12[a]	147.5[a]	126.38	115.06	163.6

Alkoxy chains = 68.69 (OCH$_2$); 31.89; 29.55; 29.32; 29.11; 26.03; 22.67; 14.09.

IR (KBr)/cm^{-1} = 1258 (C–O).

[a] Assignment uncertain.

recrystallization from ethanol. This gave white crystals, yield 60–65%.

4.5. *6-n-Decyloxy-2-(4-n-alkoxyphenylazo)-benzothiazoles (**5**)*

A mixture of 0.69 g (2.25 mmol) of 6-*n*-decyloxy-2-aminobenzothiazole (**2**) and 10 ml of concd. H$_3$PO$_4$ was gently heated and stirred until all was dissolved; it was then cooled to 0°C and 2 ml of concd. HNO$_3$ was added. Sodium nitrite 0.15 g (2.2 mmol) dissolved in a very small amount of water was added portion-wise. During this addition the temperature was kept between − 5 and 0°C. After stirring for 10 min, 2.7 mmol of alkylphenyl ether were added quickly; stirring and the low temperature were maintained for 3 h. The reaction mixture was then poured over ice, giving the crude product which was then filtered and recrystallized from ethanol, yield 60–65%.

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