Synthesis and Mesomorphic Properties of Azo Compounds Derived from Phenyl- and Thienyl-1,3,4-Thiadiazole

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Liquid Crystals, Thiadiazole, Mesomorphic Properties

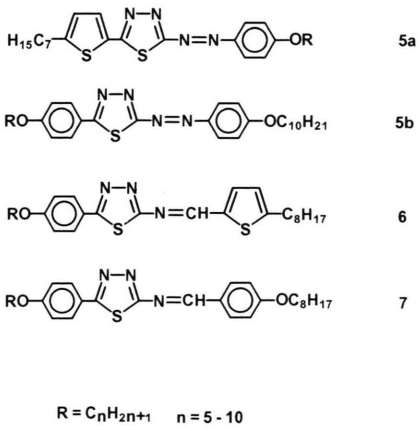
The synthesis and mesomorphic behaviour of new series of liquid crystals containing 1,3,4-thiadiazole and thiophene rings with azo central bond are reported (series **5a** and **5b**). All compounds of series **5a** exhibit enantiotropic nematic mesophase and the higher homologues (n=9–10) also show a monotropic smectic C phase. Series **5b** show dimorphism S_C–N (for n=5–7 the S_C is monotropic). These series are compared with the Schiff's bases analogues, the imine bond gives rise to similar liquid crystals phase but larger mesomorphic range.

Introduction

A great number of mesomorphic compounds containing heterocyclic units have been synthesized, and interest in such structures constantly grow [1,2]. This is not only because of the greater possibilities with heterocyclics for the design of new mesogenic molecules, but also because the insertion of heteroatoms strongly influences the formation of mesomorphic phases. The effect of heteroatoms can change considerably the polarity, polarizability and sometimes the geometry of the molecule, thereby influencing the type of mesophase, the phase transition temperatures, dielectric constants and other properties of the mesogens [3].

Heterocyclic compounds like pyridine and pyrimidine derivatives [4] are valuable liquid-crystalline materials for technical applications. It has also been reported that thiadiazole [5–8] or thiophene ring [9,10] may be incorporated into the molecular structure of calamitic mesogens.

Here we report the synthesis and mesomorphic behaviour of two homologous series of new azo compounds containing thiophene and 1,3,4-thiadiazole rings (**5a** and **5b**). We compare these compounds with the analogous Schiff's bases containing the same structural units (**6** and **7**) (Scheme 1).



Scheme 1. Structures of azo compounds and Schiff bases.

Synthesis

The reaction pathway used to prepare the azo compounds (**5a,b**) is shown in Scheme 2. Compound **1a** was synthesized starting with the acylation of the thiophene and proceeding with the reduction of the ketone moiety yielding 2-n-heptylthiophene [11,12]. The following step was the metalation with butyllithium followed by carbonation [13], yielding the 5-n-heptyl-2-thiophene carboxylic acid in good yields (70%). By esterification of the carboxylic acid the methyl ester (**1a**) was obtained [14]. Compound **1b** was synthesized by alkylation of the methyl-4-hydroxybenzoate.

Condensation of **1a,b** with 80% hydrazine hydrate [15] yielded the hydrazides **2a,b,** which react

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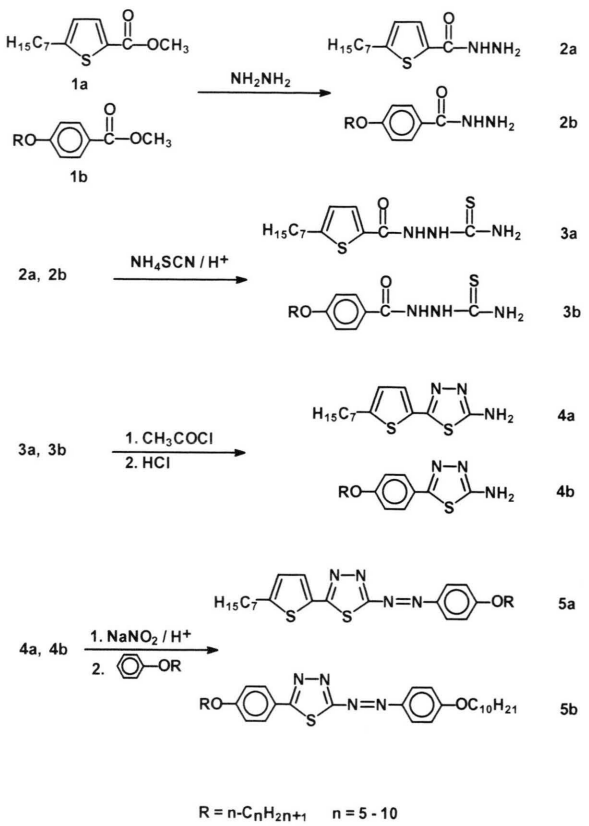

Scheme 2. Synthetic route for azo compounds.

Table I. a) Transition temperatures (°C), b) transition enthalpies (KJ/mol) and yields (%) data for the series **5a.**

n		C	S_C	N	I	Yield
5	a)	• 142.8	–	• 145.7	•	31
	b)	31.7		0.2		
6	a)	• 147.7	–	• 149.5	•	29
	b)	34.1		0.28		
7	a)	• 150.6	–	• 152.8	•	24
	b)	35.9		0.38		
8	a)	• 151.9	–	• 157.6	•	40
	b)	36.1		0.42		
9	a)	• 152.7	• (129)	• 158.5	•	55
	b)	38.3		0.88		
10	a)	• 153.8	• (130)	• 159.8	•	24
	b)	35.9		2.75		

C = Crystal, S_C = Smectic C, N = Nematic, I = Isotropic, (...) = Monotropic Transition.

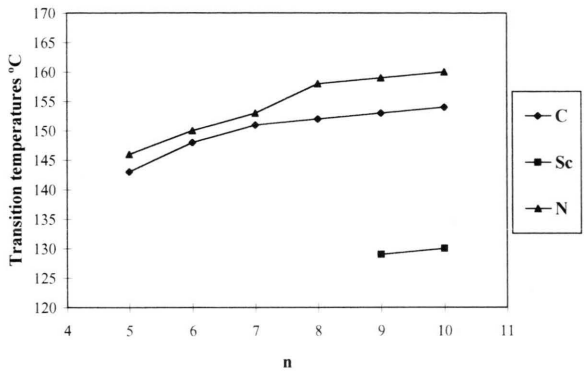

Fig. 1. The phase transition temperatures for series **5a**.

with ammonium thiocyanate in concentrated HCl medium leading to the formation of the thiosemicarbazides **3a,b** [16].

The amino-thiadiazoles **4a,b** were prepared by dehydration of **3a,b** with acetyl chloride and followed of hydrolysis of acetamido compounds [16]. The azo compounds **5a,b** were prepared by coupling between diazonium salts of the aminothiadiazoles with *n*-alkoxybenzenes [17].

Liquid Crystals Properties

The transition temperatures and transition heats were determined by DSC measurements and the transition temperatures checked using a polarizing microscope equipped with a hot stage.

The transition temperatures and enthalpies for the series **5a** are given in Table I, and the phase transition temperatures are plotted in Fig. 1. As can be seen the melting points increase with the chain length. All homologues show an enantiotropic nematic phase. The compounds with n=9 and n=10 also show a monotropic smectic C phase. The texture observed with the polarizing microscope for the nematic phase for all compounds in this series, was marble and for the monotropic smectic C phase broken fan-shaped texture was observed.

The transition temperatures and enthalpies for the series **5b** are given in Table II and the phase transition temperatures are plotted in Fig. 2. The melting points decrease with the chain length. All homologues show an enantiotropic nematic phase. The homologues with n=5–7 show a monotropic smectic C phase, and those with n=8–10 show an enantiotropic smectic C phase.

The mesophases exhibited by these compounds were identified according to their optical textures. The homologues with n=5–7 show the broken fan-

Table II. a) Transition temperatures (°C), b) transition enthalpies (KJ/mol) and yields (%) data for the series **5b.**

n		C		S_C		N		I	Yield
5	a)	•	162.1	•	(132)	•	178.3	•	73
	b)		51.95				0.79		
6	a)	•	155.6	•	(130)	•	179.0	•	46
	b)		50.06				0.66		
7	a)	•	153.7	•	(125)	•	176.5	•	34
	b)		48.49				0.58		
8	a)	•	149.9	•	156.2	•	176.4	•	61
	b)		37.46		1.13		1.15		
9	a)	•	149.5	•	159.5	•	174.0	•	75
	b)		44.41		2.17		1.09		
10	a)	•	146.8	•	162.0	•	172.9	•	76
	b)		46.92		2.76		1.45		

C = Crystal, S_C = Smectic C, N = Nematic, I = Isotropic, (...) = Monotropic Transition.

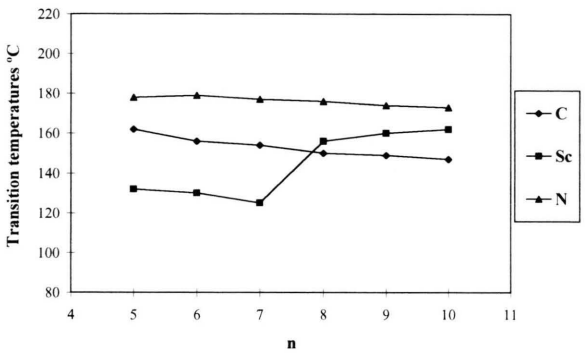

Fig. 2. The phase transition temperatures for series **5b**.

shaped texture in monotropic smectic C phase and the nematic phase showed the typical schlieren texture with characteristic two- and four-brush singularities. On cooling this phase, its colour gradually changed to finally adopt a homeotropic texture before passing into the smectic C phase. The tendency of these compounds to give rise to homeotropic alignment is noteworthy. The texture observed for the homologues with n=8–10 was schlieren, with only two-brush singularities, on both heating and cooling for smectic C phase. For nematic phase a marble texture was observed.

Series **5b** show a larger mesomorphic range than the series **5a.** Probably, the low mesophase stability of the homologues **5a** is due to the presence of the thiophene ring which produces a additional deviation from linearity and thereby a molecular curvature which disturbes the formation of stable mesophases. Using known bond angles, H. Gallardo and Y. Favarin reported that for the 2,5-disubstituted thiophene ring that there is 32° deviation from the hard rod axis of the analogous compound with a phenyl ring [18].

In order to show the different possibilities that the 1,3,4-thiadiazole ring can offer in the liquid crystals field, it is interesting to compare the mesogenic properties of these series of azo compounds with the series of Schiff's bases analogues previously synthesized and reported by us [8] (series **6** and **7**).

Table III and Fig. 3 show the mesogenic properties of Schiff's bases **6** and Table IV and Fig. 4 show the mesogenic properties of Schiff's bases **7**. These series have the same central core and show the same behaviour than series **5a,b;** the compounds containing the thiophene ring (**6**) also show a lower mesophase range than series **7**.

Table III. a) Transition temperatures (°C), b) transition enthalpies (KJ/mol) data for the series **6.**

n		C		S_C		N		I
5	a)	•	114.2	•	115.8	•	130.5	•
	b)		36.4		4.8		0.7	
6	a)	•	116.9	•	127.6	•	136.4	•
	b)		21.9		3.25		1.1	
7	a)	•	126.0	•	133.3	•	135.0	•
	b)		24.6		2.39		1.37	
8	a)	•	123.4	–		•	137.4	•
	b)		22.5				6.5	
9	a)	•	121.3	–		•	138.7	•
	b)		37.0				7.1	
10	a)	•	118.5	–		•	141.3	•
	b)		39.2				8.5	

C = Crystal, S_C = Smectic C, N = Nematic, I = Isotropic.

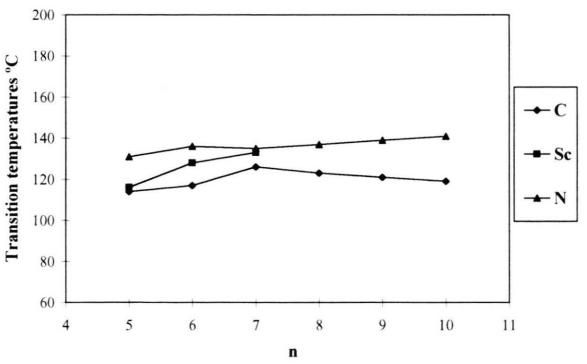

Fig. 3. The phase transition temperatures for series **6**.

Table IV. a) Transition temperatures (°C), b) transition enthalpies (KJ/mol) data for the series **7.**

n		C		S_C		N		I
5	a)	•	123.5	•	175.8	•	209.8	•
	b)		36.4		2.4		1.7	
6	a)	•	116.1	•	184.3	•	208.7	•
	b)		33.4		2.8		1.5	
7	a)	•	112.8	•	189.5	•	206.3	•
	b)		31.3		3.6		1.4	
8	a)	•	107.8	•	193.9	•	205.2	•
	b)		33.8		4.6		1.1	
9	a)	•	106.8	•	193.5	•	201.1	•
	b)		35.4		3.9		1.4	
10	a)	•	103.3	•	193.9	•	198.8	•
	b)		38.2		4.1		1.3	

C = Crystal, S_C = Smectic C, N = Nematic, I = Isotropic.

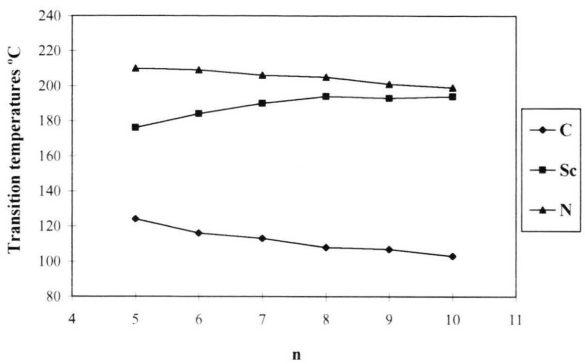

Fig. 4. The phase transition temperatures for series **7**.

However, some significant differences between both central linkages can be noted, for the imine series (**6** and **7**) the lower melting point and broader mesomorphic range can be observed, see Table III and IV. However, on the contrary the azo central linkage in the series **5a,b,** give rise the higher melting point and lower mesomorphic range, see Table I and II.

Probably, the high thermal stability of the Schiff's bases is due to that the imine linkage gives rise to a more planar structure than the azo linkage, allowing for stronger molecular interactions in the liquid crystalline phase which could explain the higher clearing temperatures of the Schiff's bases derivatives.

Experimental

The transition temperatures were determined by optical microscopy using an Ortholux Pol-BK-11 polarizing microscope equipped with a Mettler FP 800 hot stage. The transition temperatures and enthalpies were also determined from DSC measurements using a STA 625 DSC calibrated with Indium. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer.

Methyl-5-n-heptyl-2-thiophenecarboxylate (**1a**) *[14]*

To a solution of 5-*n*-heptyl-2-thiophenecarboxylic acid (38.3 g, 0.17 mol) in 500 ml of anhydrous methanol was passed through HCl gas at room temperature for 20 min. The solution was then refluxed for 18 h protected by a drying tube. The solution was evaporated, the residue was taken up on 200 ml of dichloromethane, washed with saturated Na_2CO_3 and NaCl solutions, and dried over Na_2SO_4. The solvent was evaporated and the residue was distilled to yield 34.8 g of **1a** (85%, b.p.: 105 °C/0.1 mmHg).

^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ = 7.55 (d, J=4.1 Hz, 1H, arom. H); 6.75 (d, J=4.1 Hz, 1H, arom. H); 3.80 (s, 3H, CH_3 of the ester function); 2.75 (t, J=6.45 Hz, 2H, CH_2 joined to thiophene ring); 1.65–1.30 (m, 10H, 5 CH_2); 0.85 (t, J=6.65 Hz, 3H, CH_3 of the aliphatic chain).

^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ = 160.10 (C=O); 148.82; 130.10; 127.35; 120.80 (arom. C); 50.82 (CH_3 of the ester function); 30.20–13.80 (aliph. C).

5-n-Heptyl-2-thienohydrazide (**2a**) *[15]*

A solution of **1a** (34.75 g, 0.14 mol) and excess of a solution of hydrazine hydrate (80%) in 20 ml of ethanol was heated to reflux during 8 h. The mixture was then cooled to room temperature, and the solid obtained was filtered, washed with water and recrystallized from ethanol/water (1:1), yielding 31.43 g of **2a** (90%, m.p.: 76 °C).

^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ = 8.25 (s, 1H, N–H); 7.45 (d, J=4.25 Hz, 1H, arom. H); 6.70 (d, J=4.25 Hz, 1H, arom. H); 4.15 (s, 2H, NH_2); 2.75 (t, J=6.40 Hz, 2H, CH_2 joined to thiophene ring); 1.65–1.25 (m, 10 H, 5 CH_2); 0.85 (t, J=6.60 Hz, 3H, CH_3).

^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ = 163.70 (C=O); 151.78; 133.39; 128.80; 124.95 (arom. C); 31.84; 31.48; 30.31; 29.28; 29.20; 22.65; 14.09 (aliph. C).

p-n-Alkoxybenzhydrazides (**2b**)

The series **2b** were obtained from Methyl-*p*-*n*-alkoxybenzoate (**1b**), using the same procedure given for **2a**. After recrystallization from ethanol,

white crystals were obtained, m.p.: 94–95 °C, yield 70–78%.

Spectroscopic characterization of **2b** *with n=5*

IR (KBr disk): cm^{-1}: 3310 (N–H), 3210 and 3180 (NH_2), 2950 (C_{sp3}-H), 1600 (benzene ring).

^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ = 168.28 (C=O); 161.94; 128.74; 124.56; 114.21 (arom. C); 68.11; 28.3; 24.99; 22.10; 13.99 (aliph. C).

5-n-Heptyl-2-thiophenecarbonyl-thiosemicarbazide (**3a**) *[16]*

5-*n*-Heptyl-2-thienohydrazide (**2a**) (30.0 g, 0.125 mol) was suspended in 11 ml of alcoholic hydrogen chloride solution and evaporated under reduced pressure, the residue dried by evaporation of several small amounts of alcohol and heated under reflux for 18 h with a solution of dry ammoniumthiocyanate (10.2 g, 0.14 mol) in ethanol absolute. The solid was filtered, washed several times with water and recrystallized from ethanol, yielding 24.87 g of **3a** (67%, m.p.: 177–179 °C).

^1H NMR (CD_3COCD_3, TMS, 250 MHz): δ = 9.65 (s, 1H, NH joined to C=O); 8.65 (s, 1H, NH joined to C=S); 7.60 (d, J=4.20 Hz, 1H, arom. H); 7.40 (s, 2H, NH_2); 6.90 (d, J=4.20 Hz, 1H, arom. H); 2.55 (t, J=6.40 Hz, 2H, CH_2 joined to thiophene ring); 1.70–1.30 (m, 10 H, 5 CH_2); 0.85 (t, J=6.60 Hz, 3H, CH_3).

^{13}C NMR (CD_3COCD_3, TMS, 62.9 MHz): δ = 206.38 (C=O); 185.46 (C=S); 153.40; 135.14; 130.55; 126.24 (arom. C); 32.49; 32.35; 30.81; 30.73; 28.97; 23.27; (6 C, sp^3); 14.34 (CH_3).

p-n-Alkoxybenzoylthiosemicarbazides (**3b**)

This series was prepared according to the procedure given for **3a**. The homologues were purified by recrystallization from ethanol, m.p.: 196–198 °C, yield 64–70%.

IR (KBr disk): cm^{-1}: 3550 (N–H), 3220 and 3160 (NH_2), 1650 (C=O), 1600 (benzene ring), 2920 (C_{sp3}-H).

These compounds are insoluble in common organic solvents for this reason is not possible to obtain their ^1H NMR and ^{13}C NMR spectra.

5-(5′-n-Heptyl-2′-thienyl)-2-amino-1,3,4-thiadiazole (**4a**) *[16]*

Compound **3a** (24.0 g, 0.08 mol) and acetyl chloride (250 ml) were mixed ice-cold and afterwards cautiously heated under reflux. When the vigorous reaction subside, heating was continued or 15 minutes, and water added. The insoluble material was collected, washed several times with water and recrystallized from 2-ethoxyethanol, yielding 10.6 g of the acetamido compound (41%, m.p.: 220–222 °C). This compound (10.0 g, 0.031 mol) was mixed with concentrated hydrochloric acid (52 ml) and 2-ethoxyethanol (200 ml) and then was refluxed for 18 h. The solvent was evaporated under reduced pressure and the residue was poured into concentrated sodium hydroxide solution (80 ml). The solid was filtered, washed several times with water and recrystallized from ethanol/water (1:1) yielding 4.76 g of **4a** (55%, m.p.: 140 °C).

^1H NMR ($CDCl_3$, TMS, 250 MHz): δ = 7.15 (d, J=4.10 Hz, 1H, arom. H); 6.70 (d, J=4.10 Hz, 1H arom. H); 5.95 (s, 2H, NH_2); 2.80 (t, J=6.40 Hz, 2H, CH_2 joined to thiophene ring); 1.65–1.30 (m, 10 H, 5 CH_2); 0.85 (t, J=6.60 Hz, 3H, CH_3).

^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ = 164.87; 155.76; 149.02; 130.38; 127.67; 124.67 (arom. C); 31.75; 31.60; 31.47; 30.23; 29.00; 22.64; 14.08 (aliph. C).

5-(p-n-Alkoxy)phenyl-2-amino-1,3,4-thiadiazoles (**4b**)

The homologues of amino-thiadiazoles **4b** were obtained using the same procedure given for compounds **4a**. These compounds were recrystallized from ethanol/water (4:1), m.p.: 165–170 °C, yield 70–80%.

Spectroscopic characterization of **4b** *with n=5*

IR (KBr disk): cm^{-1}: 3260, 3100 (NH_2), 1600 (benzene ring), 2920 (C_{sp3}-H).

^1H NMR (DMSO-d_6, TMS, 250 MHz): δ = 7.70 (d, J = 8.80 Hz, 2H, 2 arom. H); 7.35 (s, 2H, NH_2); 7.10 (d, J = 8.80 Hz, 2H, 2 arom. H); 4.00 (t, J = 6.50 Hz, 2H, OCH_2); 1.80–1.40 (m, 6H, $3CH_2$); 0.95 (t, J = 6.60 Hz, 3H, CH_3).

^{13}C NMR (DMSO-d_6, TMS, 62.9 MHz): δ = 167.93; 159.8; 157.36; 127.84; 123.52; 114.95 (arom. C); 67.89; 28.52; 25.51; 22.12; 13.97 (aliph. C).

2-(p-n-Alkoxyphenyl-azo)-5-(5′-n-heptyl-2′-thienyl)-1,3,4-thiadiazoles (**5a**)

General method [17]

Compound **4a** (0.50 g, 1.78 mmol) was dissolved by heating and stirring in 8 ml of 85% phosphoric acid. The solution was cooled to 0 °C in an ice bath, and then concentrated nitric acid (4 ml) and a solution of sodium nitrite (0.13 g, 1.87 mmol) in 2 ml of water was added. The mixture was stirred vigorously and maintained at below 5 °C during 10 minutes. Afterwards *n*-alkoxybenzene (1.78

mmol) was added dropwise with stirring. The yellow solid was filtered, washed several times with water and recrystallized from toluene.

The transition temperatures and yields of the series **5a** are given in Table I.

Spectroscopic characterization of **5a** *with n=5*

^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ = 8.01 (d, J=8.80 Hz, 2H, benzene ring); 7.45 (d, J=4.05 Hz, 1H, thiophene ring); 7.05 (d, J=8.80 Hz, 2H, benzene ring); 6.85 (d, J=4.05 Hz, 1H, thiophene ring); 4.10 (t, J=6.60 Hz, 2H, OCH_2); 2.85 (t, J=6.35 Hz, 2H, CH_2 joined to thiophene ring); 1.75–1.45 (m, 16H, 8 CH_2); 0.95 (t, J=6.50 Hz, 6H, 2 CH_3).

^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ = 168.85; 164.60; 162.39; 153.18; 145.51; 131.22; 130.85; 127.40; 126.25; 115.88 (arom. C); 69.39; 32.42; 32.11; 31.12; 29.68; 29.46; 28.80; 23.32; 23.11; 14.76; 14.68 (aliph. C).

2-(p-n-Decanoxyphenyl-azo)-5-(p-n-alkoxy)phenyl-1,3,4-thiadiazoles (**5b**)

Compounds **5b** were obtained from 5-(*p*-*n*-alkoxy)phenyl-2-amino-1,3,4-thiadiazoles (**4b**) and *n*-decanoxybenzene, using the same procedure given for series **5a**. The transition temperatures and yields are given in Table II.

These compounds are insoluble in common organic solvents for this reason is not possible to obtain their ^{1}H NMR and ^{13}C NMR spectra.

Acknowledgements

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