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Azo compounds and Schiff's bases derived from 5-(4-pyridyl)-2-amino-1,3,4-thiadiazole: synthesis, mesomorphic properties and structural study by semi-empirical calculations

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The synthesis and liquid crystalline properties of new Schiff's bases (series **3a–f**) and azo compounds (**4a–f**) incorporating pyridine and 1,3,4-thiadiazole rings are reported. The first homologues in the series of Schiff's bases (**3a–c**) show a monotropic mesophase and the homologues **3d–f** display an enantiotropic SmA phase. The only azo compounds to exhibit liquid crystalline properties are the homologues **4e**, **f** which show a monotropic nematic phase. These series are compared with Schiff's bases and azo compounds analogues (series **5** and **6**), previously reported by us and an AM1 study of the structure/mesomorphic property relationship is described.

1. Introduction

The study of liquid crystalline (LC) materials is of interest due to their potentially wide range of applications, such as in optical [1], electrical [2], and biological medical fields [3]. It is known that liquid crystallinity can be affected by molecular shape and conformation as well as by intermolecular interaction, and it is widely accepted that the introduction of a flexible chain into the molecules of LC materials can decrease their melting points and thus enhance the stability of the liquid crystalline phases.

During the last decades a large number of mesomorphic compounds containing heterocyclic units have been synthesized [4, 5]. Interest in these compounds arises because the inclusion of heteroatoms can cause large changes in the kind of mesophase present or in the physical properties of the phases. Heterocyclic compounds such as pyridine and pyrimidine derivatives [6] are valuable LC materials for technical applications. It has also been reported that thiadiazole [7–10] may be incorporated into the molecular structure of calamitic mesogens.

Continuing our work on the LC possibilities of thiadiazole systems, we describe in this paper the synthesis and mesogenic properties of a series of Schiff's bases (**3a–f**) and azo compounds (**4a–f**) containing pyridine and 1,3,4-thiadiazole rings. We compare these compounds with analogous Schiff's bases and azo compounds containing the same structural units (series **5** and **6**), see figure 1. Our interest in the series **3** and **4** compounds is because the pyridyl group can be considered as a H-bonding acceptor and can be used in the synthesis of LCs through the formation of intermolecular hydrogen bonds, with H-bonding donors such as carboxylic acids or phenolic compounds.

2. Synthesis

The Schiff's bases (**3a–f**) and azo compounds (**4a–f**) were synthesized according to the general procedure

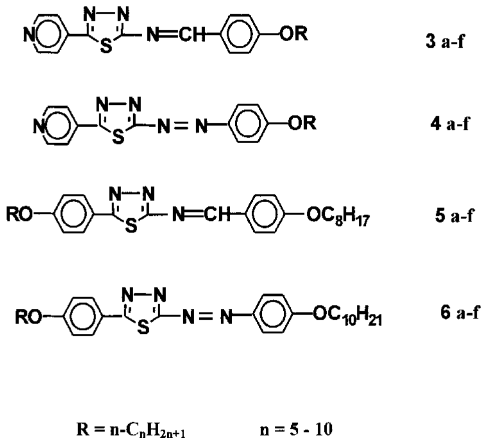

Figure 1. Structures of the compounds studied.

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outlined in the scheme. Compound **1** was synthesized by reacting 4-pyridine-carbonylhydrazine with ammonium thiocyanate in concentrated HCl [11]. The best yields were obtained for a HCl/hydrazide ratio of 2/1, because the pyridyl group also reacts with HCl to give the pyridinium chloride salt. The free pyridine derivative **1** was obtained by treatment with concentrated sodium hydroxide.

The aminothiadiazole **2** was prepared by dehydration of **1** with concentrated H_2SO_4 at 0°C [12]. Previously, we reported the synthesis of aminothiadiazoles [11] by dehydration with acetyl chloride followed by hydrolysis of acetamide compounds, however the reaction failed in our attempt to obtain compound **2** by this method.

The Schiff's bases (series **3a–f**) were prepared by condensation of **2** with an excess of the appropriate 4-*n*-alkoxybenzaldehyde [11]. The azo compounds (series **4a–f**) were obtained by the reaction of *n*-alkoxybenzenes with the diazonium salt of aminothiadiazole **2**. Sodium nitrite was used in H_3PO_4/HNO_3 medium, as described for the diazotization of 2-amino-4-methoxybenzothiazole [13] and 5-(4-*n*-alkoxy)phenyl-2-amino-1,3,4-thiadiazole [14]. The *n*-alkoxybenzaldehydes and *n*-alkoxybenzenes were synthesized by the conventional etherification of 4-hydroxybenzaldehyde and phenol, respectively [15].

3. Results and discussion

3.1. *Mesomorphic properties*

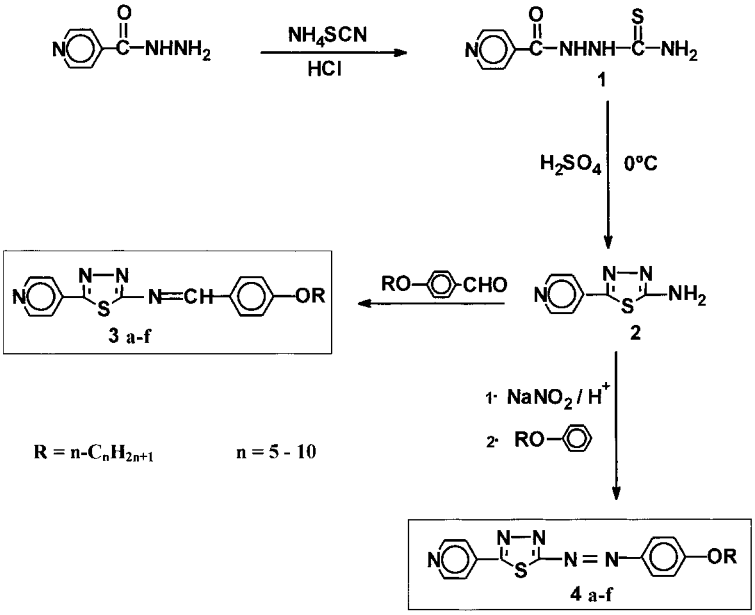
The optical, thermal and thermodynamic data for compounds **3a–f** are gathered in table 1. A graphical representation of the mesomorphic behaviour as a function of the number (n) of carbon atoms in the lateral chain is given in figure 2.

Table 1. Transition temperatures and enthalpy data for series **3a–f**: parentheses denote a monotropic transition.

Compound $R = n\text{-}C_nH_{2n+1}$	Transition	Temperature/°C	ΔH/kJ mol^{-1}
3a ($n = 5$)	Cr–I	149.5	25.2
	(I–SmA)	(141)[a]	
	(SmA–Cr)	(136.1)	−23.6
3b ($n = 6$)	Cr–I	149.3	24.7
	(I–SmA)	(149)[a]	
	(SmA–Cr)	(129.1)	−21.9
3c ($n = 7$)	Cr–I	152.4	24.0
	(I–SmA)	(150)[a]	
	(SmA–Cr)	(129.1)	−23.6
3d ($n = 8$)	Cr–SmA	147.5	21.9
	SmA–I	160.8	2.5
	I–SmA	159.8	−3.1
	SmA–Cr	135.1	−20.8
3e ($n = 9$)	Cr–SmA	141.9	23.6
	SmA–I	163.3	3.7
	I–SmA	162.2	−4.0
	SmA–Cr	127.9	−23.0
3f ($n = 10$)	Cr–SmA	142.1	25.3
	SmA–I	165.6	5.0
	I–SmA	164.6	−5.6
	SmA–Cr	130.4	−25.1

[a] Optical microscopy data.

All of the compounds in series **3a–f** show mesomorphic properties. In each case a smectic A (SmA) mesophase is observed. The first members of the series ($n = 5$–7) show a monotropic SmA mesophase over a similar temperature range (approximately 20°C), except for



Scheme. Synthetic route for Schiff's bases (series **3a–f**) and azo compounds (series **4a–f**).

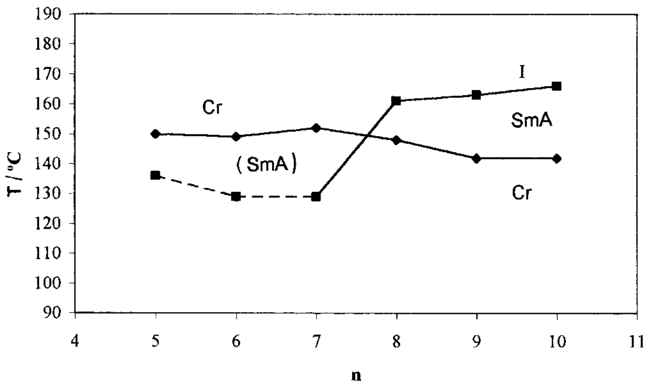


Figure 2. Plot of transition temperatures versus the number of carbon atoms (n) in the alkyl chain (R) of series **3** compounds.

Table 2. Transition temperatures and enthalpy data for series **4a–f**: parentheses denote a monotropic transition.

Compound $R = n$-C$_n$H$_{2n+1}$	Transition	Temperature/°C	ΔH/kJ mol^{-1}
4a ($n = 5$)	Cr–I (I–Cr)	155.2 142.2	35.2 −36.5
4b ($n = 6$)	Cr–I I–Cr	155.3 140.3	35.5 −36.1
4c ($n = 7$)	Cr–I I–Cr	157.4 140.0	35.9 −36.3
4d ($n = 8$)	Cr–I I–Cr	150.5 140.1	35.0 −36.6
4e ($n = 9$)	Cr–I (I–N) (N–Cr)	144.0 (136.0)^a (115.5)	35.9 −30.8
4f ($n = 10$)	Cr–I (I–N) (N–I)	140.1 (136.0)^a 115.1	36.0 −30.2

^{a} Optical microscopy data.

homologue with $n = 5$ which has a smaller range (4.9°C). The other homologues ($n = 8$–10) show an enantiotropic SmA mesophase. The SmA–I transition temperature increases with increase in chain length, leading to a broadening of the SmA mesophase range, (13.3, 21.4 and 23.5°C for $n = 8$, 9 and 10 respectively). On slow cooling from the isotropic melt, these homologues clearly show the existence of a SmA phase.

The SmA phase was determined from textural observations (see § 3.2) by thermal microscopy under a polarizing microscope using heating and cooling rates of 1°C min^{-1}. Phase transition temperatures observed by thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms. Curiously, the enthalpy of the SmA–I transition shows a steady increase as the number of carbon atoms in the alkoxy chain increases, corresponding to an average value of around 1.2 kJ mol^{-1} for each methylene group. This result illustrates the importance of the influence of the terminal chain length, both on the SmA–I transition and on mesomorphic stability.

All of the compounds **4a–f** exhibit a Cr–I transition and only the homologues with $n = 9$, 10 form a monotropic nematic phase directly on slow cooling (1°C min^{-1}) of the isotropic liquid (see table 2).

The Schiff's bases (series **3**) and the azo compounds (series **4**) have the same central core and the same alkoxy chains, however some significant differences between their central linkages can be noted. The imine compounds **3a–f** display monotropic and enantiotropic mesomorphic properties; in contrast, the azo compounds (**4a–f**) do not show enantiotropic mesophases, and only the homologues with $n = 9$, 10 display a monotropic nematic phase.

Many Schiff's bases that consist of a rigid core structure and have only one terminal alkoxy chain have been reported by Byron *et al.* [16] and Gray *et al.* [17]. However, the Schiff's bases **3a–f** synthesized by us are heterocyclics and display only a SmA phase, whereas those reported by these authors are homocyclics and show SmB and SmA phases.

Crystal structure determinations on the analogous benzylideneanilines, have been reported by Bürgi and Dunitz [18]; from X-ray studies they conclude that the imine linkage lies almost exactly in a plane, but that the aniline rings are twisted out of this plane. On this basis, Byron *et al.* [16] have assumed a non-coplanar structure for the Schiff's bases reported by them, which pack together in the smectic layers in a juxtaposed arrangement with a cooperative rotational arrangement in the SmB phase and free rotation in the SmA phase. So we may assume that in the molecules of the Schiff's bases **3a–f** the juxtaposed arrangement and the cooperative rotation are absent and a free rotation of the molecules must exist, this could explain the existence of the SmA as a unique orthogonal phase.

We have determined the structure of the benzylideneaniline reported by Bürgi and Dunitz [18] using AM1 semi-empirical calculations. Our results are in agreement with those obtained by the X-ray studies, the benzene rings in this benzylideneaniline are non-coplanar. In contrast to this, structural determinations using the same semi-empirical method show that in the Schiff's bases **3a–f** the aromatic rings are coplanar with the central imine linkage. The same structural results have been obtained for the azo compounds **4a–f**.

The differences in mesomorphic stability between the Schiff's bases **3a–f** and the azo compounds **4a–f** can be explained by considering the rigidity of the Schiff's bases in the liquid crystalline phase. These compounds have a higher rotational barrier around the thiadiazole ring and imine linkage than the corresponding azo compounds (see § 3.3). We conclude that the Schiff's bases have a more rigid core than the azo compounds, leading to high thermal stability; similar results have been reported for the Schiff's bases and azo compounds containing crown ether units [19].

In order to show the different possibilities that the 1,3,4-thiadiazole ring can offer in the LC field, it is interesting to compare the mesogenic properties of these Schiff's bases (series **3**) and azo compounds (series **4**) with analogous Schiff's bases (series **5**) and azo compounds (series **6**), previously synthesized and reported by us [10, 14].

Tables 3 and 4 show the mesogenic properties of Schiff's bases **5a–f** and azo compounds **6a–f**, respectively. These series have the same central core and show a similar behaviour to series **3a–f** and series **4a–f** compounds; also the azo compounds **6a–f** have a lower thermal stability than the Schiff's bases **5a–f**. However, there are some significant differences between the new and earlier compounds.

The imine series **5** has lower melting points and broader mesomorphic ranges (approximately 95°C) than the imine series **3** and all the homologues display an enantiotropic dimorphism SmC–nematic. The azo compounds **6** also show dimorphism SmC–nematic, but for homologues with $n = 5$–7 the SmC phase is monotropic; they also have a higher thermal stability than the azo compounds **4**.

Table 3. Transition temperatures and enthalpy data for series **5a–f**.

Compound $R = n\text{-}C_nH_{2n+1}$	Transition	Temperature/°C	ΔH/kJ mol^{-1}
5a ($n = 5$)	Cr–SmC	123.5	36.4
	SmC–N	175.8	2.4
	N–I	209.8	1.7
5b ($n = 6$)	Cr–SmC	116.1	33.4
	SmC–N	184.3	2.8
	N–I	208.7	1.5
5c ($n = 7$)	Cr–SmC	112.8	31.3
	SmC–N	189.5	3.6
	N–I	206.3	1.4
5d ($n = 8$)	Cr–SmC	107.8	33.8
	SmC–N	193.9	4.6
	N–I	205.2	1.1
5e ($n = 9$)	Cr–SmC	106.8	35.4
	SmC–N	193.5	3.9
	N–I	201.1	1.4
5f ($n = 10$)	Cr–SmC	103.3	38.2
	SmC–N	193.9	4.1
	N–I	198.8	1.3

Table 4. Transition temperatures and enthalpy data for series **6a–f**: parentheses denote a monotropic transition.

Compound $R = n\text{-}C_nH_{2n+1}$	Transition	Temperature/°C	ΔH/kJ mol^{-1}
6a ($n = 5$)	Cr–N	162.1	51.95
	N–I	178.3	0.79
	(N–SmC)	(132)[a]	
6b ($n = 6$)	Cr–N	155.6	50.06
	N–I	179.0	0.66
	(N–SmC)	(130)[a]	
6c ($n = 7$)	Cr–N	153.7	48.49
	N–I	176.5	0.58
	(N–SmC)	(125)[a]	
6d ($n = 8$)	Cr–SmC	149.9	37.46
	SmC–N	156.2	1.13
	N–I	176.4	1.15
6e ($n = 9$)	Cr–SmC	149.5	44.41
	SmC–N	159.5	2.17
	N–I	174.0	1.09
6f ($n = 10$)	Cr–SmC	146.8	46.92
	SmC–N	162.0	2.76
	N–I	172.9	1.45

[a] Optical microscopy data.

The main difference between Schiff's bases **3** and azo compounds **4** and the analogous Schiff's bases **5** and azo compounds **6** is in their structures. The former have a pyridine unit at the end of a rigid core and have only one lateral chain, whereas the latter have a benzene instead of a pyridine unit, two lateral chains and a greater molecular length. We conclude that the compounds containing pyridine (series **3** and **4**) are not long enough or sufficiently polarizable to produce stable mesophases in comparison with series **5** and **6**. On the other hand, the lateral chains play an important role in the stabilization of mesophases.

3.2. *Textures observed by polarizing optical microscopy*

The mesophases exhibited by Schiff's bases **3a–f** and azo compounds **4a–f** were identified from their optical textures which were observed by optical microscopy, using the classification systems reported by Sackmann and Demus [20] and Gray and Goodby [21]. The SmA phase was characterized by the formation of bâtonnets that coalesce to form a fan-shaped texture. Mechanical stress on such a sample leads to the formation of a homeotropic texture. A mielinic texture was also formed, characteristic of the SmA phase (see figure 3). The monotropic nematic mesophase of the azo homologues with $n = 9$, 10 was characterized by the formation of schlieren textures and the typical nematic droplets.

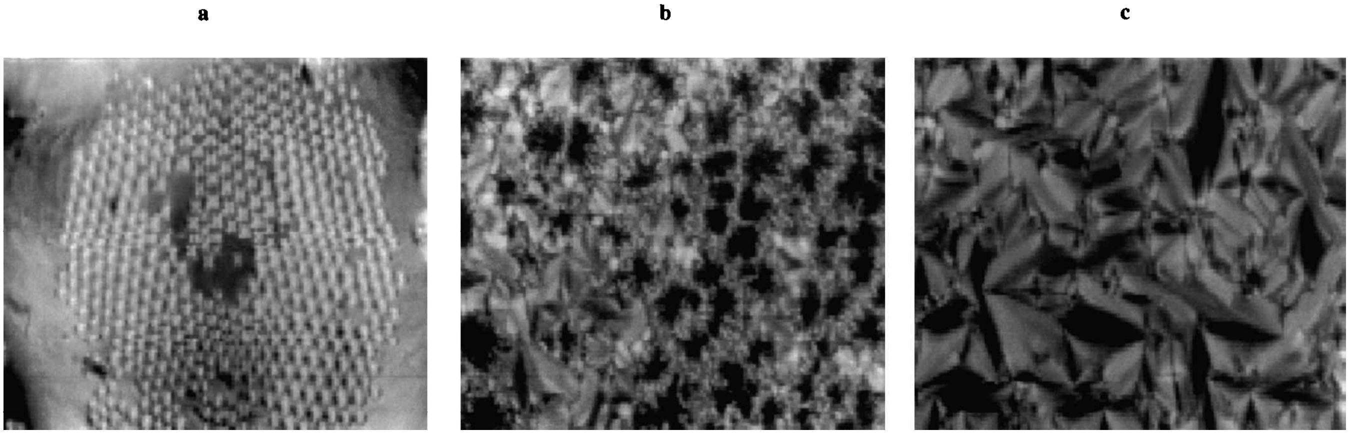


Figure 3. Mesophase textures of compound **3f** ($n=10$) obtained by cooling. (*a*) Mielinic texture at 163°C; (*b*) transition from mielinic to fan-shaped texture at 157°C; (*c*) fan-shaped texture at 147°C.

3.3. *Structure/mesomorphic property relationships*

As previously noted, Schiff's bases **3** exhibit the monotropic SmA phase for homologues with $n=5$–7 and the enantiotropic SmA phase for homologues with a longer alkoxy chain ($n=8$–10), whereas none of the azo compounds of series **4** display enantiotropic mesophases, and only homologues with $n=9$, 10 exhibit a monotropic nematic mesophase. However, different behaviour is observed for the Schiff's bases **5** and azo compounds **6** analogues, which have a more stable mesomorphic properties than shown by series **3** and **4**. However, both series of azo compounds (**4** and **6**) are less stable than the corresponding series of Schiff's bases (**3** and **5**).

In order to obtain structural information we performed semi-empirical calculations at level AM1 [22], implemented on the GAUSSIAN 94W program [23]. We used the derivatives with a methoxy terminal chain as molecular models, and see that the most stable conformation in both Schiff's bases **3** and azo derivatives **4** is that with a coplanar arrangement between the heterocyclic unit and the central bridge. Figure 4 shows two conformations adopted for these derivatives: 4(*a*) corresponds to a conformation for $\phi_2=0°$ designated 's-*cis*', 4(*b*) corresponds to a conformation for $\phi_2=180°$ designated 's-*trans*'. The 's-*cis*' conformation is more linear than the 's-*trans*' conformation, both in Schiff's bases **3** and azo compounds **4**. The same conformations are shown by derivatives **5** and **6**.

We also studied the rotational barrier around the C(heterocyclic)–N(exocyclic) bond (ϕ_2). A significant difference was found in the stabilization between the extreme values of 's-*cis*' and 's-*trans*' conformers. The 's-*trans*' have a higher energy than 's-*cis*' conformers, 7.5 and 3.5 kcal mol^{-1} for Schiff's bases and azo compounds, respectively (figure 5). Similar results were previously reported for chelating imines derived from

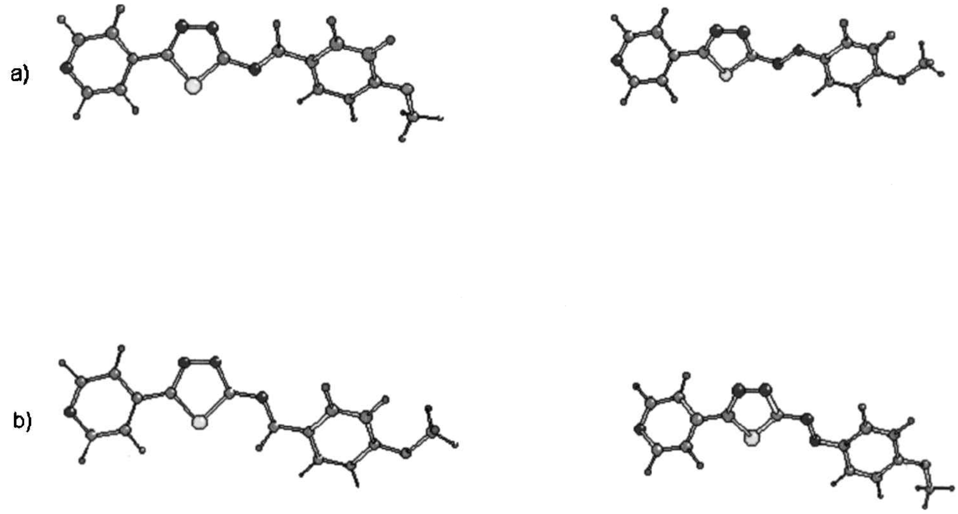


Figure 4. Representation of the two coplanar conformations of the Schiff's bases **3** and azo compounds **4**. (*a*) Conformation of the 's-*cis*' for $\phi_2=0°$; (*b*) conformation of the 's-*trans*' for $\phi_2=180°$.

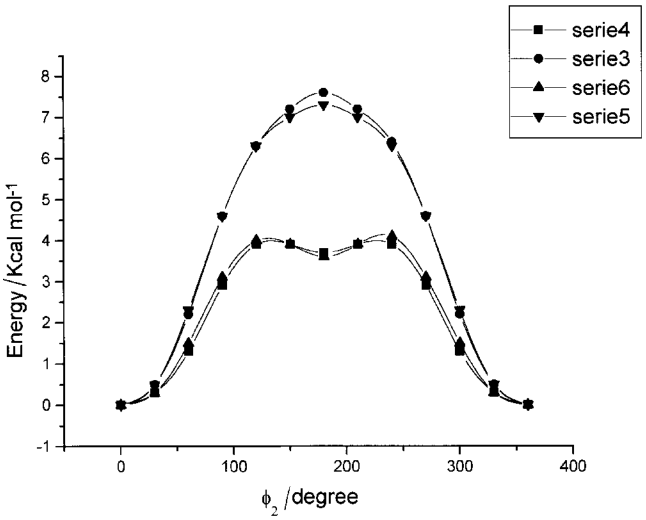


Figure 5. Potential energy curve describing the rotational barrier around the C(heterocyclic)–N(exocylic) bond (ϕ_2).

thiadiazoles and oxadiazoles [11]. These values correspond to $\phi_2 = 180°$ and 90°, respectively. The azo compounds thus have a lower rotational barrier and in this case the 's-*trans*' conformers should have a greater population than in the Schiff's bases derivatives.

From these significant differences we conclude that 's-*cis*' is the most stable conformation both for the Schiff's bases and for azo compounds. However, Schiff's bases have a major rotational barrier and also show a hindered rotation around ϕ_2, and consequently a major rigid core linearity; this could explain the different behaviour exhibited for these series in comparison with the series of azo compounds. On the other hand, the mesomorphic differences between Schiff's bases **3** and **5**, and between azo compounds **4** and **6**, can be explained by considering their molecular length. Compounds **5** and **6** have two flexible alkoxy chains with a greater molecular length, and consequently have more stable mesophases.

4. Experimental

The structures of the compounds were confirmed by ^{1}H NMR, ^{13}C NMR (Bruker AC-250P) and FTIR (Nicolet 550) spectra. The transition temperatures and textures of mesophases 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 investigated by differential scanning calorimetry (DSC) using a Rheometric DSC-V calorimeter. Samples were encapsulated in aluminium pans and studied at a scanning rate of 5°C min^{-1} on both heating and cooling cycles. The instrument was calibrated using an indium standard (156.6°C, 28.44 J g^{-1}). The purity of the final products was evaluated by thin layer chromatography and elemental analysis (Perkin Elmer PE 240) (table 5).

4.1. *4-Pyridine-carbonylthiosemicarbazide (1)* [11]

4-Pyridine-carbonylhydrazine (10.0 g, 73 mmol) was suspended in 180 ml of alcoholic hydrogen chloride solution (12 ml of HCl 37% and 168 ml of ethanol) and the mixture evaporated under reduced pressure. The residue was dried by evaporation of several small amounts of alcohol and heated under reflux for 18 h with a solution of dry ammonium thiocyanate (5.95 g, 78 mmol) in 300 ml of ethanol absolute. The solid was filtered, then suspended in water and neutralized with concentrated NaOH, then filtered, washed several times with water and recrystallized from ethanol/water (1/1), yielding white needles (7.58 g, 53%), m.p. 230°C. ^{1}H NMR (DMSO-d$_6$, TMS, 250 MHz): $\delta = 10.82$

Table 5. Elemental analysis for series **3a–f** and **4a–f**.

	C/%		H/%		N/%		S/%	
Empirical formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Schiff's bases								
3a $C_{19}H_{20}N_4SO$	64.78	64.56	5.68	5.88	15.90	16.20	9.10	9.12
3b $C_{20}H_{22}N_4SO$	65.58	65.50	6.01	6.11	15.29	15.11	8.75	8.80
3c $C_{21}H_{24}N_4SO$	66.32	66.40	6.31	6.42	14.73	14.60	8.43	8.56
3d $C_{22}H_{26}N_4SO$	67.01	66.21	6.59	6.67	14.20	14.30	8.13	8.28
3e $C_{23}H_{28}N_4SO$	75.66	75.59	6.86	6.90	13.75	13.80	7.85	7.90
3f $C_{24}H_{30}N_4SO$	68.25	68.36	7.10	7.15	13.26	13.31	7.59	7.61
Azo compounds								
4a $C_{18}H_{19}N_5SO$	61.20	61.19	5.38	5.26	19.82	19.90	9.08	9.20
4b $C_{19}H_{21}N_5SO$	62.13	62.11	5.72	5.80	19.06	19.21	8.73	8.87
4c $C_{20}H_{23}N_5SO$	63.00	63.03	6.03	6.13	18.36	18.50	8.40	8.60
4d $C_{21}H_{25}N_5SO$	63.80	63.82	6.32	6.41	17.71	17.93	8.11	8.24
4e $C_{22}H_{27}N_5SO$	64.56	64.60	6.60	6.68	17.10	17.38	7.83	7.90
4f $C_{23}H_{29}N_5SO$	65.26	65.31	6.85	6.70	16.54	16.70	7.57	7.70

(s, 1H, NH joined to C=O); 9.56 (s, 1H, NH joined to C=S); 8.80 (d, $J = 2.5$ Hz, 2H, 2 arom. H); 7.87 (d, $J = 2.5$ Hz, 2H, 2 arom. H); 7.90 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6, TMS, 62.9 MHz): $\delta = 182.82$ ($\underline{C}$=O); 165.0 ($\underline{C}$=S); 139.9 (quaternary arom. C); 150.4; 122.1 (arom. C). IR (KBr disk): cm^{-1} = 3267.9 (NH); 3054.4 (NH_2); 2938.0 (Csp^2−H); 1686.3 (C=O); 1544.6 (C=C).

4.2. *5-(4-Pyridyl)-2-amino-1,3,4-thiadiazole (**2**)* [12]

Concentrated sulphuric acid (120 ml) was cooled to 0°C and stirred while compound **1** (6 g, 30.6 mmol) was added portionwise. The mixture was stirred for 3 h in the cold and then allowed to warm to room temperature over a 1 h period. The solution was poured onto crushed ice and adjusted to pH 12 with concentrated sodium hydroxide. The precipitated product was collected and recrystallized from water yielding white needles (3.82 g, 70%), m.p. 240°C. ^{1}H NMR (DMSO-d_6, TMS, 250 MHz): $\delta = 8.7$ (s, 2H, NH_2); 7.85 (d, $J = 2.5$ Hz, 2H, 2 arom. H); 7.75 (d, $J = 2.5$ Hz, 2H, 2 arom. H). ^{13}C NMR (DMSO-d_6, TMS, 62.9 MHz): $\delta = 170.3$; 154.5; 138.1 (quaternary arom. C); 150.9; 120.6 (arom. C). IR (KBr disk): cm^{-1} = 3314; 3272 (NH_2); 3046 (Csp^2−H); 1646 (C=C).

4.3. *5-(4-Pyridyl)-2-(4-n-alkoxy)-benzylideneamino-1,3,4-thiadiazoles (**3a–f**)*

General method [11]: A mixture of aminothiadiazole **2** (0.5 g, 2.81 mmol) and 4-*n*-alkoxybenzaldehyde (14.1 mmol) was heated in an oil bath at 180°C for 1 h. The residue was cooled and crystallized from ethanol and then purified by column chromatography on silica gel using hexane/ethyl acetate (7/3) as eluent.

n	5	6	7	8	9	10
Yields (%)	67	70	81	92	95	95.

Spectroscopic characterization of homologue **3f** with $n = 10$. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): $\delta = 8.97$ (s, 1H, N=CH); 8.80 (d, $J = 5.3$ Hz, 2H, pyridine ring); 8.0 (d, $J = 8.7$ Hz, 2H, benzene ring); 7.87 (d, $J = 5.3$ Hz, 2H, pyridine ring); 7.05 (d, $J = 8.7$ Hz, 2H, benzene ring); 4.10 (t, $J = 6.51$ Hz, 2H, OCH_2); 1.87 (m, 2H, $OCH_2C\underline{H}_2$); 1.33 (m, 14H, 7 CH_2); 0.93 (t, $J = 6.88$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): $\delta = 175.3$; 164.1; 163.8; 137.6; 127.0 (quaternary arom. C); 166.8 (N=$\underline{C}$H); 150.7; 132.7; 121.0; 115.1 (arom. C); 68.5 (O$\underline{C}H_2$); 31.8; 29.5; 29.3; 29.0; 25.9; 22.6; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 3020 (Csp^2−H); 2926 (Csp^3−H); 1592 (C=C and C=N).

4.4. *5-(4-Pyridylazo)-5-(4-n-alkoxy)phenyl-1,3,4-thiadiazoles (**4a–f**)*

General method [13, 14]: Aminothiadiazole **2** (0.5 g, 2.81 mmol) was dissolved by heating and stirring in 12 ml of 85% phosphoric acid. The solution was cooled in an ice bath, and then concentrated nitric acid (5 ml) and a solution of sodium nitrite (0.38 g, 5.5 mmol) in 2 ml of water were added. The mixture was stirred vigorously and maintained below 5°C during 10 min. *n*-Alkoxybenzene (2.81 mmol) was then added dropwise with stirring. The orange solid was filtered, washed several times with water and recrystallized from ethanol; it was then purified by column chromatography on silica gel using hexane/ethyl acetate (7/3) as eluent.

n	5	6	7	8	9	10
Yields (%)	19	14	12	32	17	16.

Spectroscopic characterization of homologue **4d** with $n = 8$. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): $\delta = 8.85$ (d, $J = 4.57$ Hz, 2H, pyridine ring); 8.09 (d, $J = 9.07$ Hz, 2H, benzene ring); 7.97 (d, $J = 4.57$ Hz, 2H, pyridine ring); 7.08 (d, $J = 9.07$ Hz, 2H, benzene ring); 4.12 (t, $J = 6.54$ Hz, 2H, OCH_2); 1.88 (m, 2H, $OCH_2C\underline{H}_2$); 1.33 (m, 10H, 5 CH_2); 0.93 (t, $J = 6.35$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): $\delta = 180.7$; 165.7; 164.9; 146.2; 137.5 (quaternary arom. C); 150.7; 127.2; 121.5; 115.3 (arom. C); 68.8 (O$\underline{C}H_2$); 31.8; 29.2; 29.0; 25.9; 22.6; 14.1 (aliph. C). IR (KBr disk): cm^{-1} = 3046 (Csp^2−H); 2977 (Csp^3−H); 1589 (C=C and N=N).

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