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Synthesis, mesomorphic properties and structural study by semi-empirical calculations of amides containing the 1,3,4-thiadiazole unit

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The synthesis and liquid crystalline properties of a new series of amides (series **2a–f**, **3a–d** and **4a–d**) incorporating pyridine and 1,3,4-thiadiazole rings are reported. No homologues of the series **2** show mesomorphic properties. In the series **3** only the highest homologues (**3d**) displays an enantiotropic SmA mesophase; the compound **3c** exhibits a monotropic SmA mesophase, and the homologues **3a**,**b** display no liquid crystal properties. The amides **4b–d** display an enantiotropic SmA phases and the first homologue (**4a**) exhibit only crystal–isotropic transition. These series are compared with previously reported Schiff's bases and amide analogues. A structural study by AM1 semi-empirical calculation is also described.

1. Introduction

In the well established classical concept of calamitic liquid crystals a molecular geometry as close to linearity as possible is required, which is generally obtained by using aromatic, heteroaromatic or aliphatic rings as mesogenic units. On the other hand, some functional central bridging groups have proven to be very useful to promote mesomorphic properties. For example, the ester and imine groups are some of the most commonly used [1–4]. The amide group is infrequently encountered in liquid crystal derivatives because, in general, it gives rise to significantly higher intermolecular interactions that often preclude mesomorphic behaviour [5].

The 2-amino-1,3,4-thiadiazoles are interesting systems for the design and synthesis of liquid crystalline compounds with a classical rod-like structure. The introduction of a thiadiazole ring within the central core of calamitic molecules strongly influences their mesomorphic behaviour due (though not only) to the dipolar moment associated with the heterocyclic ring.

We have previously reported the synthesis and mesomorphic properties of Schiff's bases, azo compounds and amides derived from 5-(4-*n*-alkoxy)phenyl-2-amino-1,3,4-thiadiazole. These liquid crystals consist of a conjugated aromatic central core and two terminal flexible chains [6–9]. More recently, we have reported mesogenic Schiff's bases and non-mesogenic azo compounds, with one terminal flexible chain derived from 5-(4-pyridyl)-2-amino-1,3,4-thiadiazole [10]. In this paper we present three new series of amides (series **2**, **3** and **4**) incorporating pyridine, thiadiazole rings and only one terminal flexible chain (alkoxy or alkyl chains), which have been synthesized in order to study the effect of (1) the amide group, (2) the length of the rigid core, and (3) the presence of alkoxy or alkyl chains on the mesogenic properties. Also, we compare these amides with analogous Schiff's bases and with amides previously reported by us (series **6**, see scheme) [9, 10].

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2. Synthesis

The synthesis of the amides **2**–**4** is outlined in the scheme.

The aminothiadiazoles **1** and **5** were synthesized starting with the corresponding hydrazide, leading to the formation of the corresponding thiosemicarbazide; this was followed by dehydration, according to the methods described in references [10, 11]. Commercial acid chlorides (Merck) were used in the formation of the amides; the synthesis of the amides **6a–f** was reported in [9].

3. Results and discussion

3.1. *Mesomorphic properties*

None of the compounds in series **2** show mesomorphic behaviour; only crystal–isotropic (Cr–I) transitions are observed, indicating that the rigid core is too short or insufficiently polarizable to produce mesogenic behaviour. In series **3** only the homologue **3d** displays an enantiotropic smectic A (SmA) mesophase; compound **3c** exhibits

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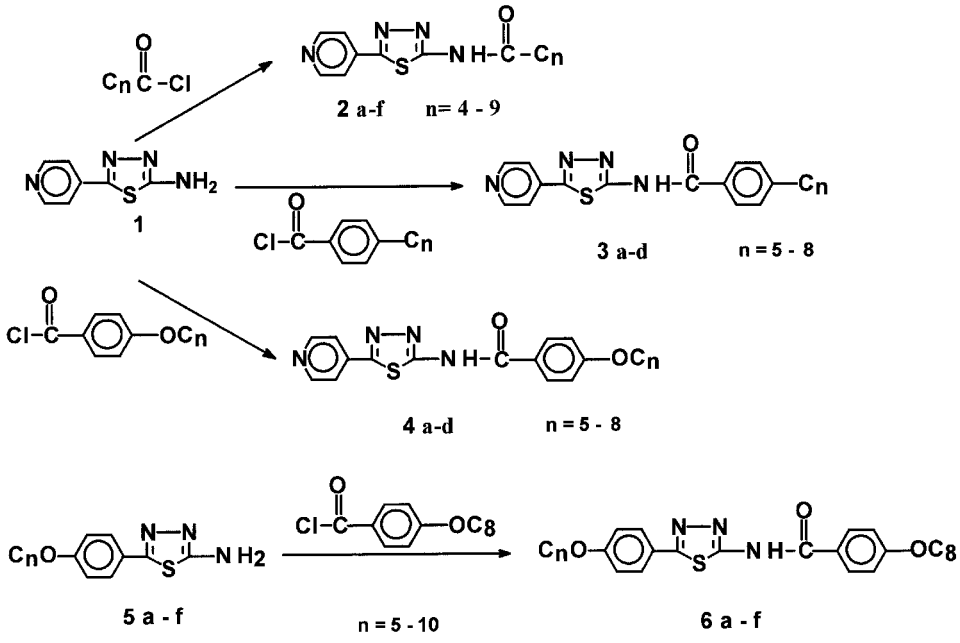

Scheme. Synthetic route for amides.

a monotropic SmA phase, and the homologues **3a–b** show no liquid crystalline properties. In contrast to this, in series **4** only the first homologue (**4a**) does not show mesomorphism, exhibiting only a Cr–I transition. The higher homologues (**4b–d**) display an enantiotropic SmA mesophase.

The optical, thermal and thermodynamic data for the compounds of series **3** and **4** 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 also presented in figure 1.

The series **3** and **4** have a similar melting points, however there are other significant differences between these series. The amides of series **4** have higher thermal stabilities and broader mesomorphic ranges (approximately 40°C) than those of the amides of the series **3**. The homologues **4b–d** are enantiotropic liquid crystals (LC), whereas compound **3b** is not a LC; compound **3c** exhibits a short monotropic mesomorphic range (6.5°C); compound **3d** is an enantiotropic LC, but has a lower mesomorphic range (12°C) on heating than its analogues **4b–d**. On cooling, the SmA–Cr transition of compound **3d** occurs at a lower temperature than the melting point.

These series have the same rigid core and the same number of carbon atoms in the lateral chain. The unique difference is that in series **3** the lateral chains are alkyl chains whereas in series **4** they are alkoxy chains. This could explain the higher thermal stability of the amides of series **4**. Probably, a lateral interaction giving rise to

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for series **3a–d** and **4a–d** compounds. Phase transition temperatures and corresponding enthalpies were determined by the 2nd heating and cooling DSC scans at heating and cooling rates of 5°C min^{-1}.

Compound	Transition	Temperature	ΔH
3a ($n = 5$)	Cr–I	242.1	45.3
	I–Cr	220.2	36.0
3b ($n = 6$)	Cr–I	231.5	39.8
	I–Cr	202.3	28.2
3c ($n = 7$)	Cr–I	206.5	31.8
	I–SmA	195.5	3.5
	SmA–Cr	189.0	21.2
3d ($n = 8$)	Cr–SmA	195.4	29.8
	SmA–I	207.4	4.4
	I–SmA	206.2	4.5
	SmA–Cr	172.4	15.0
4a ($n = 5$)	Cr–I	248.4	43.9
	I–Cr	240.3	27.6
4b ($n = 6$)	Cr–SmA	211.3	18.7
	SmA–I	250.6	6.7
	I–SmA	247.5	6.5
	SmA–Cr	207.4	18.3
4c ($n = 7$)	Cr–SmA	209.5	19.8
	SmA–I	256.1	8.5
	I–SmA	254.1	9.0
	SmA–Cr	205.8	19.7
4d ($n = 8$)	Cr–SmA	211.2	14.1
	SmA–I	250.3	5.3
	I–SmA	248.2	5.5
	SmA–Cr	207.9	14.0

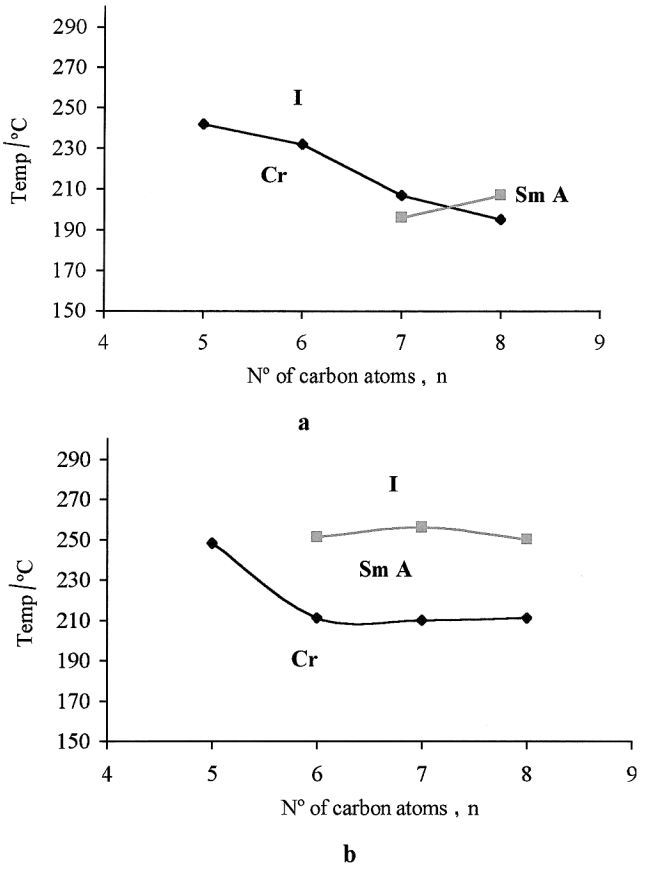

Figure 1. Plot of transition temperature versus the number of carbon atoms (n) in the alkyl chain for: (a) series **3** and (b) series **4**.

a layered smectic order is more favoured for the compounds of series **4** as compared with their analogues in series **3**, due to a major volume occupied by the flexible melted alkoxy chains and a higher polarizability due to the presence of the oxygen atom.

We now compare the mesogenic properties of the series **4** amides with analogous Schiff's bases [10], see figure 2.

All homologues of the Schiff's bases display an SmA phase as well as the homologues of the amides **4b–d**. However, the Schiff's bases display monotropic ($n = 5$–7) and enantiotropic ($n = 8$–10) mesomorphism with a lower mesomorphic range than the series **4** amides. The amides in this series have higher thermal stability than the Schiff's bases. This can be explained by taking into account the formation of H-bonding between molecules

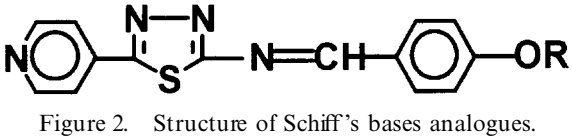

Figure 2. Structure of Schiff's bases analogues.

of the amides. This parallel molecular arrangement would encourage smectic mesomorphism by providing additional lateral intermolecular attraction and by lining up molecules in a layered order [12–14]. For amides **4b–d** the layered smectic order is more favoured than for the Schiff's bases; this is fully compatible with a molecular arrangement resulting from intermolecular H-bonding.

It is also interesting to compare the mesogenic properties of the amides of series **3** and series **4** with the analogous amides of series **6a–f** (see the scheme), previously reported by us [9]. The compounds of series **6** show a different mesomorphic behaviour from the corresponding compounds of series **3** and **4**, displaying nematic (N) and smectic C (SmC) mesomorphism in the whole range of n studied. In this case, no SmA mesophase is observed; see table 2 and figure 3.

The compounds of series **6** have lower melting points and broader mesomorphic ranges (approximately 100°C) than the compounds of series **3** and **4**. On the other hand, as the length of alkoxy chain increases, the thermal stability of the SmC phase increases and the thermal stability of the N phase decreases. These results indicate that the amides **6** also follow the common rule that the SmC phase is more favoured in molecules with longer flexible lengths [15].

The difference between amides **3**, **4** and the analogous amides **6** is their structure. The former have a pyridine unit at the end of a rigid core and only one lateral chain; the latter have benzene instead of a pyridine unit, two

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) data of series **6a–f** compounds. Phase transition temperatures and corresponding enthalpies were determined by the 2nd heating and cooling DSC scans at heating and cooling rates of 5°C min^{-1}.

Compound	Transition	Temperature	ΔH
6a ($n = 5$)	Cr–SmC	164.8	20.7
	SmC–N	241.8	3.8
	N–I	260.5	1.2
6b ($n = 6$)	Cr–SmC	153.9	23.1
	SmC–N	246.3	5.0
	N–I	259.6	1.3
6c ($n = 7$)	Cr–SmC	149.3	19.9
	SmC–N	247.5	5.6
	N–I	256.4	1.7
6d ($n = 8$)	Cr–SmC	146.6	17.0
	SmC–N	247.7	5.0
	N–I	254.3	1.3
6e ($n = 9$)	Cr–SmC	139.5	14.1
	SmC–N	246.2	3.6
	N–I	250.8	0.8
6f ($n = 10$)	Cr–SmC	140.7	16.3
	SmC–N	245.0	3.8
	N–I	248.3	0.9

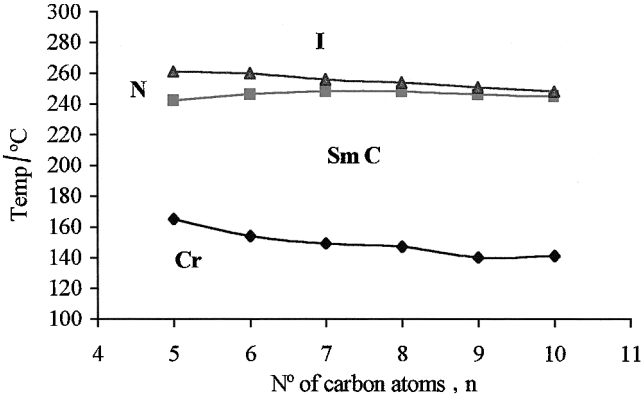

Figure 3. Plot of transition temperature versus the number of carbon atoms (n) in the alkyl chain for series **6**.

lateral chains, and a greater molecular length. We conclude that the compounds containing pyridine (series **3** and **4**) are too enough or insufficiently polarizable to produce stable mesophases in comparison with series **6**. On the other hand, the lateral alkoxy chains play an important role in the stabilization of mesophases.

The occurrence of a tilted SmC mesophase in the compounds of series **6** opens an interesting possibility for further studies, such as the introduction of a chiral terminal alkoxy chain in the calamitic structure in order to obtain chiral mesophases (cholesteric, tilted smectic) which may exhibit interesting electro-optical properties. On the other hand, the compounds of the series **2**, **3** and **4** have a pyridine unit in their structures and can be used as a H-bonding acceptor in the synthesis of LCs through the formation of intermolecular hydrogen bonds. Research in this direction is already in progress.

3.2. *Textures observed by polarizing optical microscopy*

The mesophases exhibited by amides **3** and **4** were identified according to their optical textures which were observed by optical microscopy, using the classification systems reported by Sackmann and Demus [16], and Gray and Goodby [17]. The SmA phase was determined from textural observations by thermal microscopy under a polarizing microscope using a heating and cooling rate of 1°C min^{-1}. Phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms.

The SmA phase was characterized by the formation of bâtonnets that coalesce to form mielinic textures; homeotropic zones were also observed. The SmC mesophase exhibited by the amides of series **6** was identified by the appearance of a broken focal-conic texture coexisting with the fine four-brush schlieren texture. The N phase showed the characteristic marbled texture and the typical schlieren texture with two- and four-brush singularities.

3.3. *Semi-empirical calculations*

In order to obtain structural information we performed semi-empirical calculations at level AM1, implemented using the GAUSSIAN 94W program [18]. Figure 4 shows two conformations adopted for the amides **2**, **3** and **6** (*s-trans* and *s-cis*). In all cases the *s-trans* conformations are more linear than *s-cis* conformations. However, the *s-cis* are more stable than *s-trans* conformations (approximately 20 kJ mol^{-1}). Amides **4** show similar behaviour. This stability can be explained by considering the electrostatic interactions between the amide group and the thiadiazole ring, which are minimized when the compounds adopt the *s-cis* conformation. The *s-cis* conformation of the amides **6** is more linear than the *s-cis* conformation of the amides **2–4**. This fact could explain the higher mesomorphic stability exhibited by these compounds (series **6**). On the other hand the *s-cis* conformation of compounds **2** is less linear than the amides **3**, **4** and **6**, which could explain their non-mesomorphic behaviour.

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.

4.1. *5-(4-Pyridyl)-2-amino-1,3,4-thiadiazole (1)*

This compound was synthesized according to a previously reported method [10].

4.2. *5-(4-Pyridyl)-2-n-alkylamido-1,3,4-thiadiazole (**2a–f**)* [19]

A mixture of 1.12 mmol of 5-(4-pyridyl)-2-amino-1,3,4-thiadiazole (**1**) and 1.22 mmol of *n*-alkyl acid chloride in 20 ml of acetonitrile and 1 ml of triethylamine was heated under reflux for 4 h and then poured into a mixture of water and ice. The product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (7/3) as eluent, and then recrystallized from ethanol.

Compound	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
Yield %	62	77	66	68	73	70
m.p. °C	245	225	203	205	170	190

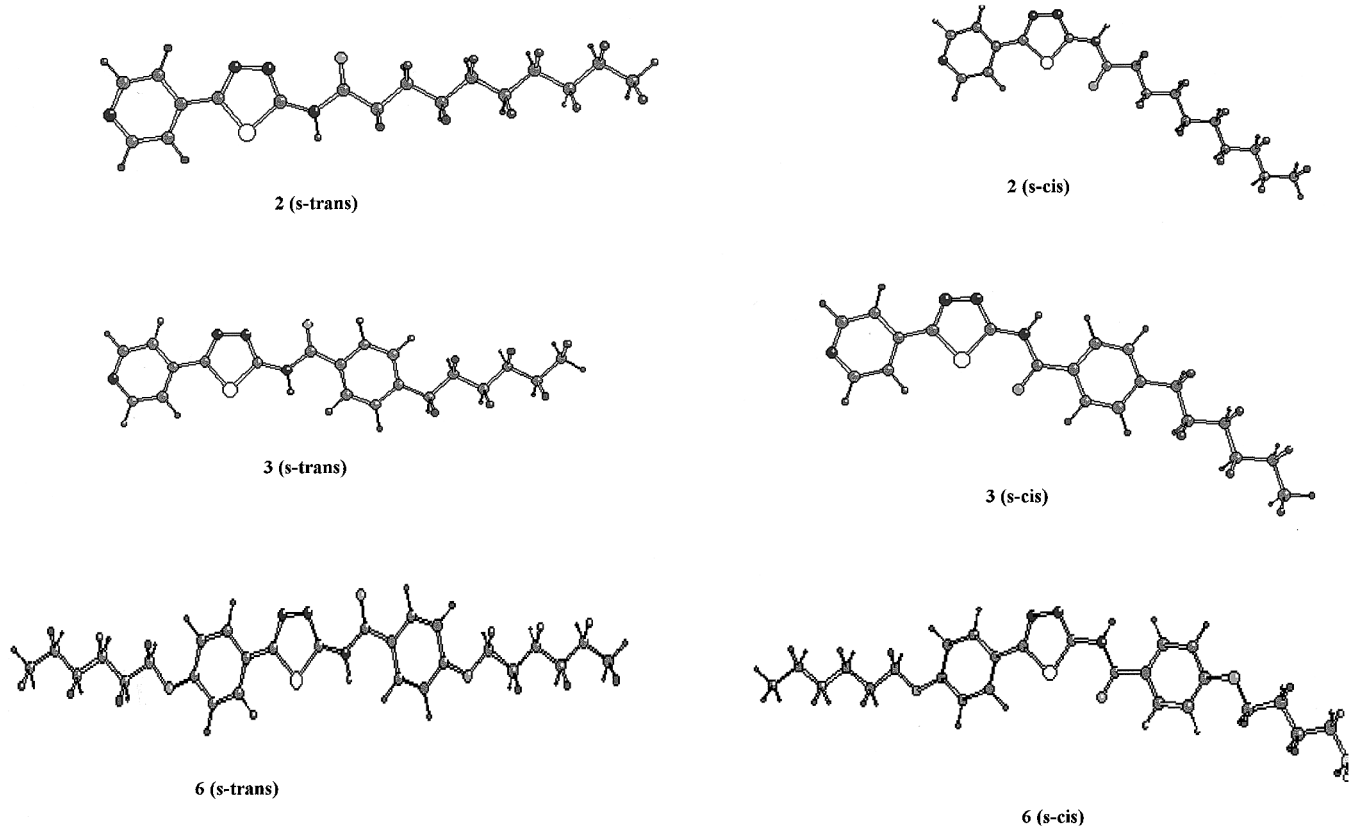

Figure 4. Diagram of *s-trans* and *s-cis* conformations of amides **2**, **3** and **6**.

Spectroscopy characterization of homologue **2d** with $n = 7$: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz); δ ppm = 13.48 (s, 1H, NH); 8.71 (d, $J = 5.25$ Hz, 2H, arom. H); 7.74 (d, $J = 5.25$ Hz, 2H, arom. H); 2.80 (t, $J = 7.50$ Hz, 2H, $COCH_2$); 1.80–1.30 (m, 10 H, 5 CH_2); 0.82 (t, $J = 6.70$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz); δ ppm = 172.2 (C=O); 161.3; 160.3; 137.5 (quaternary arom. C); 150.7; 120.8 (arom. C); 36.4; 31.7; 29.3; 28.9; 25.4; 22.6; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 3438 (NH); 3149 (Csp^2-H); 2925 (Csp^3-H); 1698 (C=O); 1557 (C=C).

4.3. *5-(4-Pyridyl)-2-(4-n-alkyl)phenylamido-1,3,4-thiadiazole (**3a–d**)*

The synthesis procedure was similar to that given for compounds **2a–f**.

Compound	**3a**	**3b**	**3c**	**3d**
Yield %	55	67	66	77

Spectroscopy characterization of homologue **3c** with $n = 7$: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 12.80 (s, 1H, NH); 8.80 (d, $J = 5.69$ Hz, 2H, pyridine ring); 8.39 (d, $J = 8.50$ Hz, 2H, benzene ring); 7.90 (d, $J = 5.60$ Hz, 2H, pyridine ring); 7.45 (d, $J = 8.49$ Hz, 2H, benzene ring); 2.05 (t, $J = 6.60$ Hz, 2H, CH_2 joined to benzene ring); 1.95–1.30 (m, 10 H, 5 CH_2); 0.95 (t, $J = 6.40$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 171.8 (C=O); 165.0; 164.8; 160.3; 140.8; 125.3 (quaternary arom. C); 155.7; 136.0; 121.9; 114.8 (arom. C); 36.1; 32.8; 30.9; 28.5; 27.1; 23.9; 14.7 (aliph. C). IR (KBr disk): cm^{-1} = 3438 (NH); 3145 (Csp^2-H); 2930 (Csp^3-H); 1670 (C=O); 1556 (C=C).

4.4. *5-(4-Pyridyl)-2-(4-n-alkoxy)phenylamido-1,3,4-thiadiazole (**4a–d**)*

The synthesis procedure was similar to that given for compounds **2a–f**.

Compound	**4a**	**4b**	**4c**	**4d**
Yield %	71	92	87	65

Spectroscopy characterization of homologue **4c** with $n = 7$: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 12.54 (s, 1H, NH); 8.77 (d, $J = 5.51$ Hz, 2H, pyridine ring); 8.27 (d, $J = 8.73$ Hz, 2H, benzene ring); 7.82 (d, $J = 5.67$ Hz, 2H, pyridine ring); 7.03 (d, $J = 8.77$ Hz, 2H, benzene ring); 4.05 (t, $J = 6.48$ Hz, 2H, OCH_2); 1.82–1.10 (m, 10 H, 5 CH_2); 0.89 (t, $J = 6.50$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 170.8 (C=O); 164.8; 163.6; 159.8, 137.7; 122.8 (quaternary arom. C); 150.8; 130.9; 120.8; 114.6 (arom. C); 68.5

(OCH_2); 31.7; 29.1; 26.0; 22.6; 14.1 (aliph. C). IR (KBr disk): cm^{-1} = 3437 (NH); 3145 (Csp^2-H); 2931 (Csp^3-H); 1668 (C=O); 1550 (C=C).

4.5. *5-(4-n-Alkoxy)phenyl-2-amino-1,3,4-thiadiazole (**5a–f**)*

These compounds were synthesized according to the method previously reported by us [11].

4.6. *5-(4-n-Alkoxy)phenyl-2-(4-n-octyloxy)-phenylamido-1,3,4-thiadiazole (**6a–f**)*

These compounds were synthesized according to the method previously reported by us [9].

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