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Synthesis and mesomorphic properties of esters derived from Schiff's bases containing 1,3,4-thiadiazole

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Two homologous series of esters derived from Schiff's bases containing the 1,3,4-thiadiazole unit (series **3** and **5**) were synthesized and their liquid crystalline properties investigated by optical microscopy and differential scanning calorimetry. Depending on the position occupied by the carbonyl group, the smectic A phase was observed in series **3** and nematic phase in series **5**.

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1. Introduction

The introduction of a thiadiazole ring into the principal structure of heteroaromatic systems opens the possibility of generating new mesogenic units. The heteroatoms can cause considerable changes of polarity, polarizability and geometry of the molecules and influence the type and phase transition temperatures of the mesophases [1–12].

We have previously reported the synthesis and mesomorphic properties of Schiff's bases, azo compounds and amides derived from 2-amino-1,3,4-thiadiazole derivatives. These liquid crystals consist of a conjugated aromatic central core and two terminal alkoxy flexible chains [7–10]. We have also reported mesogenic Schiff's bases and amides with only one terminal flexible chain [11, 13].

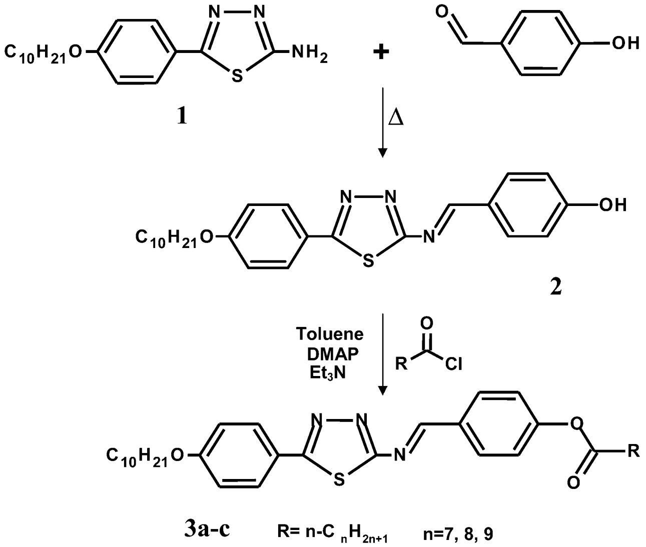
The correlation between chemical structure and mesomorphic properties is one of the most important problems in liquid crystals science. An understanding of the influence of different structural elements of the molecules on the physico-chemical characteristics of mesomorphic organic compounds allows chemists to synthesize liquid crystals with required properties. In this context, it was considered interesting to synthesize two new homologous series of Schiff's bases containing the 1,3,4-thiadiazole ring (series **3a**–**c** and series **5a**–**c**), in which one substituent is a terminal alkoxy group with the number of carbon atoms kept constant at $n=10$, while the other terminal substituent is an flexible ester chain (either benzoate-like or alkanoate-like). In order to predict the mesogenic behaviour of these compounds, to visualize the role of the ester group in the terminal flexible chain, and to study the effect of the position of the carbonyl group in the ester chain, we compare these compounds with analogous Schiff's bases previously reported by us [11].

2. Synthesis

The mesogenic Schiff's bases, series **3a**–**c** and series **5a**–**c**, were synthesized according to the general procedures outlined in schemes 1 and 2, respectively.

The aminothiadiazole **1** was synthesized starting with the corresponding hydrazide, leading to the formation of the corresponding thiosemicarbazide, this was followed by dehydration, according to the methods previously described [11, 14].

The Schiff's base **2** was prepared by condensation of



Scheme 1. Synthetic route for esters of series **3a**–**c**.

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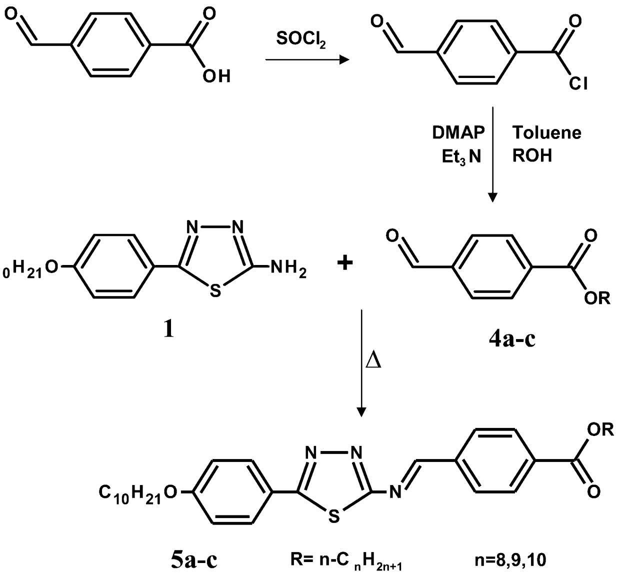


Scheme 2. Synthetic route for esters of series **5a**–**c**.

1 with an excess of 4-hydroxybenzaldehyde [14]. By esterification of **2** with the appropriate carboxylic acid chloride, the homologues series **3a**–**c** was obtained.

The homologues series **5a**–**c** was obtained by condensation of **1** with an excess of the appropriate *n*-alkyl-4-formylbenzoate (series **4a**–**c**) which were synthesized by the conventional esterification of 4-formylbenzoic acid [15].

3. Results and discussion

3.1. *Mesomorphic properties*

All compounds in the series **3a**–**c** show mesomorphic properties. In each case an enantiotropic smectic A (SmA) mesophase is observed, while the homologues of the series **5a**–**c** display an enantiotropic nematic phase which shows an odd–even alternation effect for the crystal to nematic and nematic to isotropic transition. Compounds of series **3a**–**c** have a higher melting point and a lower clearing temperature than the compounds of series **5a**–**c**.

The optical, thermal and thermodynamic data for the compounds of series **3** and **5** are gathered in the table; a graphical representation of the mesomorphic behaviour is presented in figure 1.

Compounds of series **3a**–**c** and **5a**–**c** have the same central rigid core and the same alkoxy chain. The difference between these series is in their lateral ester chains. The results show that the position of the carbonyl function of the ester group has a profound influence on the mesogenic properties. While compounds of series **5** exhibit a nematic phase, compounds of series **3** display a SmA phase. Clearly, the carbonyl group connected away from the aromatic rigid core (series **3a**–**c**) favours the SmA phase, indicating that the lateral dipolar interactions associated with terminal ester chain dipoles dominate phase structure in smectic liquid crystals [16].

Table. Transition temperatures and enthalpies for compounds of series **3a**–**c** and **5a**–**c**. Cr = crystal, SmA = smectic A, I = isotropic.

Compound, $R = n\text{-}C_nH_{2n+1}$	Transition	Temperature/°C	ΔH/kJ mol^{-1}
3a (*n* = 7)	Cr–SmA	140.2	10.2
	SmA–I	151.7	7.5
3b (*n* = 8)	Cr–SmA	117.7	12.5
	SmA–I	157.6	7.7
3c (*n* = 9)	Cr–SmA	134.5	8.3
	SmA–I	159.0	8.0
5a (*n* = 8)	Cr–N	118.1	27.5
	N–I	175.7	4.1
5b (*n* = 9)	Cr–N	107.1	17.3
	N–I	170.7	2.9
5c (*n* = 10)	Cr–N	120.1	31.7
	N–I	182.1	4.9

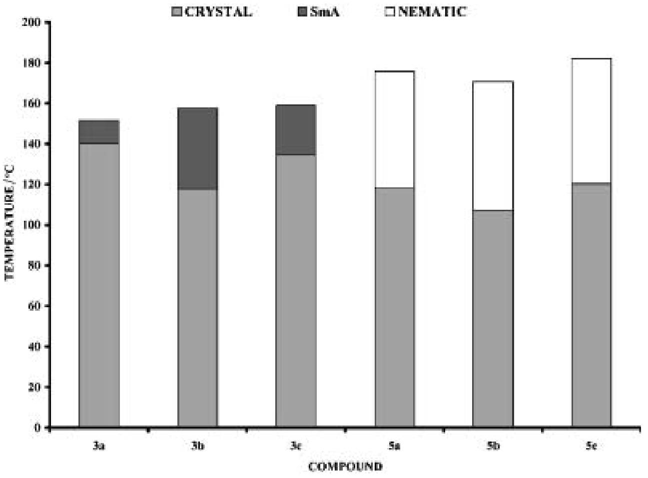
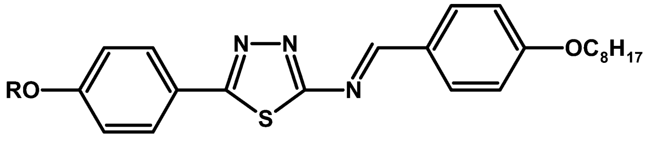


Figure 1. Plot of transition temperature versus the number of carbon atoms in the ester chain of series **3** and **5** compounds.

It is interesting to compare the mesomorphic properties of the Schiff's bases of series **3** and **5** with the analogous Schiff's bases (series **6a**–**f**), previously reported by us [11] (see figure 2), which have the following mesomorphic properties (transition temperatures in °C):

n = 5	Cr	123.5	SmC	175.8	N	209.8	I
n = 6	Cr	116.1	SmC	184.3	N	208.7	I
n = 7	Cr	112.8	SmC	189.5	N	206.3	I
n = 8	Cr	107.8	SmC	193.9	N	205.2	I
n = 9	Cr	106.8	SmC	193.5	N	201.1	I
n = 10	Cr	103.3	SmC	193.9	N	198.8	I.



6a-f R=n-C_nH_{2n+1} n=5-10

Figure 2. Structure of series **6** compounds.

The compounds of series **6** have the same central rigid core as those of the series **3** and **5**. The main difference between the Schiff's bases **3** and **5**, and the analogous Schiff's bases **6**, is in their lateral flexible chains. The former have an alkoxy chain and an ester chain at the end of the rigid core, whereas the latter have two lateral alkoxy chains.

Compounds of series **6** show a different mesomorphic behaviour from the corresponding compounds of series **3** and **5**, displaying smectic C (SmC) and nematic (N) mesomorphism in the whole range of *n* studied. In this case, no SmA mesophase is observed. The imines of series **6** have lower melting points and broader mesomorphic ranges (approximately 90°C) than the imines of series **3** and **5**. On the other hand, as the alkoxy chain length increases, the thermal stability of the SmC phase increases and the thermal stability of the N phase decreases. These results indicate that the imines **6** also follow the common rule that the SmC phase is more favoured in molecules with longer flexible lengths [17].

Probably, a lateral interaction giving rise to a layered smectic order is more favoured for the compounds of series **3** and **6** as compared with their analogues in series **5**, due to a best packing molecular arrangement which has an effect on the strength of the dipolar interactions [18].

3.2. *Textures observed by polarizing optical microscopy*

The mesophases exhibited by Schiff's bases of series **3** and **5** were identified according to their optical textures, which were observed by optical microscopy, using the classification systems reported by Sackmann and Demus [19] and Gray and Goodby [20].

The SmA and nematic phases were determined from textural observations by thermal microscopy under a polarizing microscope using heating and cooling cycles. Phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms.

The SmA phase of series **3** was characterized by the formation of a typical focal-conic fan texture. The nematic phase of series **5** showed a characteristic schlieren texture with two- and four-brush singularities (see figure 3).

3.3. *Structure/mesomorphic property relationship*

In order to obtain structural information we performed semi-empirical calculations at AM1 level, implemented on the GAUSSIAN 94W series of programs [21, 22]. Several initial conformations were optimized, for the three series of compounds (**3**, **5** and **6**). In general no great difference of energy was found between the different conformations; in all cases, less than 0.5 kcal mol^{-1}.

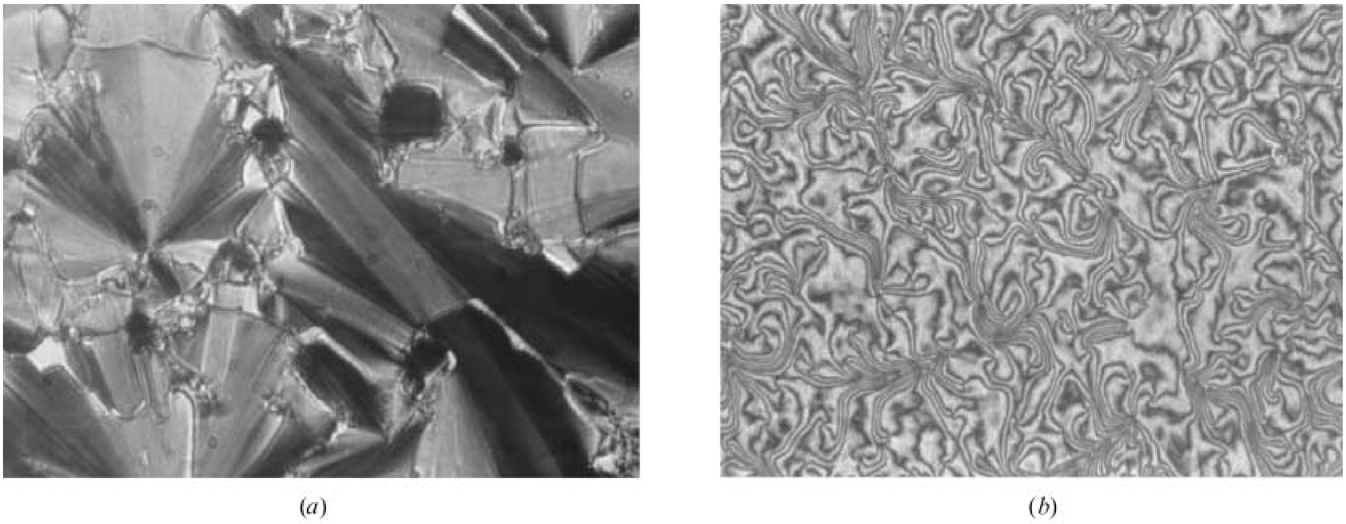


Figure 3. Mesophase textures obtained by cooling. (*a*) Focal-conic fan (SmA) at 152°C of compound **3b**; (*b*) schlieren texture at 160°C of compound **5b**.

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Figure 4 shows the most stable conformation of the compounds **3**, **5** and **6**. In series **5** the lateral ester chain produces a great loss of linearity, therefore lateral dipolar interactions are not favoured and consenquently a layered smectic order is prevented. In contrast to this, in series **3** and **6** the conformations maintain linearity, which could explain the occurrence of smectic mesomorphism in these series.

4. Experimental

The structures of the compounds were confirmed by ^{1}H NMR, ^{13}C NMR (Bruker AC-250P) and FTIR (Nicolet 550) spectra. Transition temperatures and mesophase textures were determined by optical microscopy using an Ortholux Pol BK-11 polarizing microscope equipped with a Mettler FP 800 hot stage.

Transition temperatures and enthalpies were investigated by differential scanning calorimetry using a Rheometric DSC-V calorimeter. Samples were encapsulated in aluminium pans and observed at a scanning rate of 5°C min^{-1}, on heating or cooling. 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-n-Decyloxy)phenyl-2-amino-1,3,4-thiadiazole (**1**)*

This compound was synthesized according to reference [14].

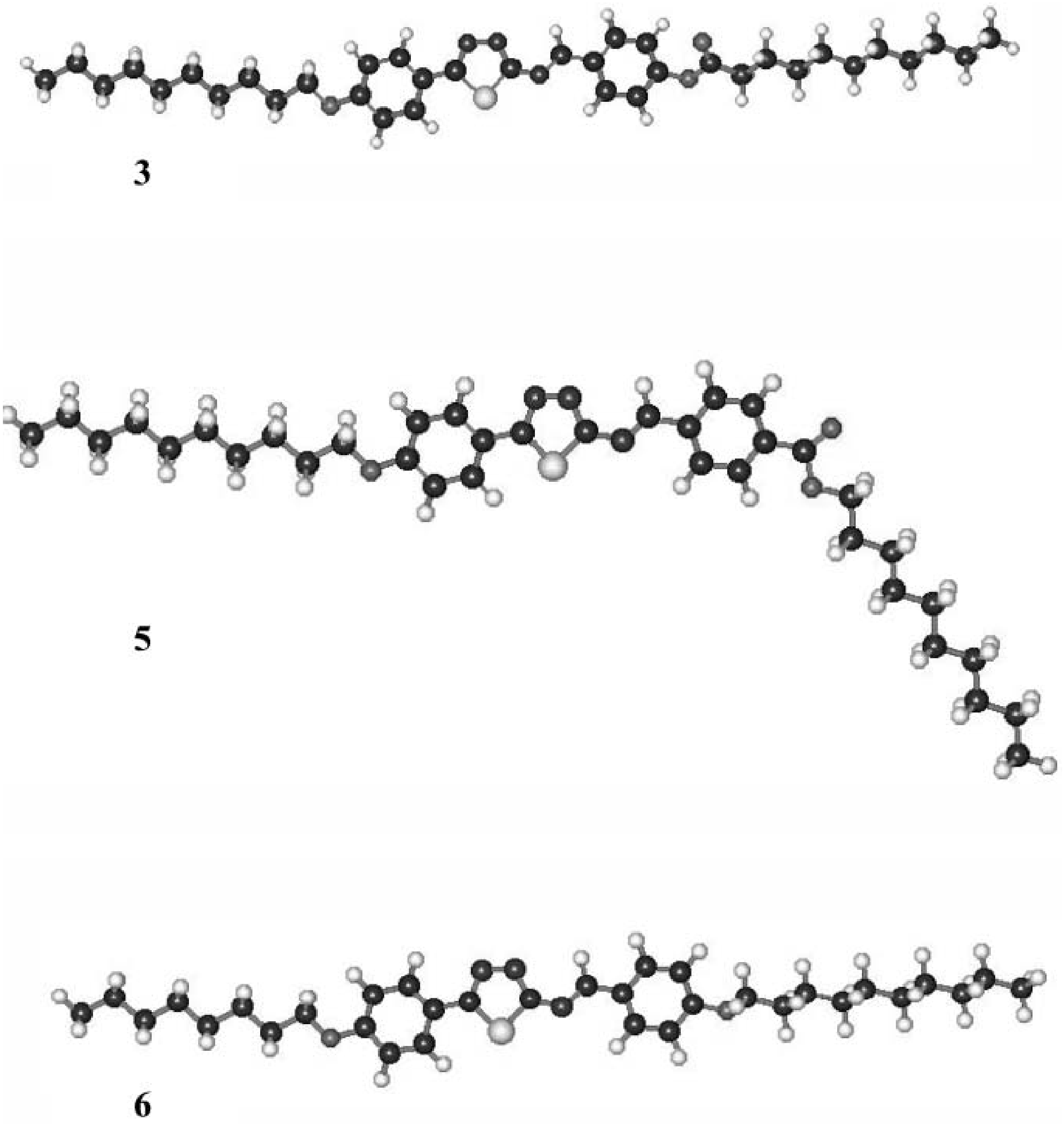

Figure 4. Diagram of the most stable conformation of the compounds **3**, **5** and **6**.

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4.2. *5-(4-n-Decyloxy)phenyl-2-(4-hydroxy)benzylideneamino-1,3,4-thiadiazole (**2**)*

This compound was prepared from 4-hydroxybenzaldehyde and 5-(4-*n*-decyloxy)phenyl-2-amino-1,3,4-thiadiazole (**1**) according to the reported procedure [14] as follows. A mixture of **1** (1.5 mmol, 0.5 g) and 4-hydroxybenzaldehyde (2.25 mmol 0.28 g) was heated in an oil bath at 120°C for 30 min. The residue was cooled and crystallized from ethanol; yield 56%, m.p 220°C. ^{1}H NMR (DMSO-d$_6$, TMS, 250 MHz): $\delta = 9.55$ (s, 1H, N$=$C$\underline{\text{H}}$); 8.03 (d, $J = 6.95$ Hz, 2H, arom. H); 7.96 (d, $J = 6.92$ Hz, 2H, arom. H); 7.21 (d, $J = 8.77$ Hz, 2H, arom. H); 7.05 (d, $J = 8.67$ Hz, 2H, arom: H); 4.14 (t, $J = 6.38$ Hz, 2H, OC$\underline{\text{H}}_2$); 1.20 (m, 16H, 8 CH$_2$); 0.94 (t, $J = 6.90$ Hz, 3H, CH$_3$). ^{13}C NMR (DMSO-d$_6$, TMS, 62.9 MHz): $\delta = 167.2$ (N$=$CH); 162.7; 160.8; 131.6; 127.5; 115.6; 114.8 (quaternary arom. C); 132.2; 128.5; 115.9; 115.1 (arom. C); 67.8 (CH$_2$O); 30.8; 28.5; 28.3; 25.0; 21.6 (aliph. C); 13.4 (CH$_3$). IR (KBr disk): cm$^{-1} = 3421$ (OH); 3022 (Csp^2–H); 2923 (Csp^3–H); 1569 (C$=$C).

4.3. *4-{[5-(4-n-Decyloxyphenyl-1,3,4-thiadiazol-2-yl)imino]methyl}phenylalkanoates (**3a–c**)*

The general method of reference [15] was used. To a solution of 0.238 mmol (0.1 g) of **2**, 0.032 g of 4-dimethylaminopyridine (DMAP) and 1 ml of triethylamine in 20 ml of dry toluene, was added 0.238 mmol of the corresponding alkanoyl chloride. The mixture was stirred for 24 h at room temperature. The organic product was extracted with ether, and the ethereal phase washed twice with water (50 ml) and once with 20 ml of brine. The organic phase was dried over anhydrous Na$_2$SO$_4$, the solvent was evaporated and the residue purified by recrystallization from ethanol. The following yields were obtained: **3a** 50%, **3b** 47%, **3c** 55%.

3a, $R = n$-C$_7$H$_{15}$. ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): $\delta = 8.89$ (s, 1H, N$=$C$\underline{\text{H}}$); 7.97 (d, $J = 8.60$ Hz, 2H, arom. H); 7.83 (d, $J = 8.84$ Hz, 2H, arom. H); 7.18 (d, $J = 8.62$ Hz, 2H, arom. H); 6.94 (d, $J = 8.90$ Hz, 2H, arom. H); 3.95 (t, $J = 6.56$ Hz, 2H, OC$\underline{\text{H}}_2$); 2.50 (t, $J = 6.50$ Hz, 2H, O$_2$CC$\underline{\text{H}}_2$); 1.21 (m, 26H, 13 CH$_2$); 0.80 (t, $J = 6.70$ Hz, 6H, 2 CH$_3$). ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): $\delta = 173.5$ (C$=$O); 168.9 (N$=$CH); 167.5; 165.3; 161.7; 144.5; 133.3; 122.8 (quaternary arom. C); 131.7; 128.5; 122.5; 115.0 (arom. C); 68.4 (CH$_2$O); 34.5 (O$_2$CC$\underline{\text{H}}_2$); 31.5; 29.5; 29.1; 26.0; 22.7 (aliph. C); 14.1 (2 CH$_3$). IR (KBr disk): cm$^{-1} = 1749$ (C$=$O); 3028 (Csp^2–H); 2921 (Csp^3–H); 1609 (C$=$C).

3b, $R = n$-C$_8$H$_{17}$. ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): $\delta = 8.88$ (s, 1H, N$=$C$\underline{\text{H}}$); 7.98 (d, $J = 8.56$ Hz, 2H, arom. H); 7.84 (d, $J = 8.81$ Hz, 2H, arom. H); 7.19 (d, $J = 8.59$ Hz, 2H, arom. H); 6.92 (d, $J = 8.79$ Hz, 2H, arom. H); 3.97 (t, $J = 6.39$ Hz, 2H, OC$\underline{\text{H}}_2$); 2.53 (t, $J = 6.40$ Hz, 2H, O$_2$CC$\underline{\text{H}}_2$); 1.21 (m, 28H, 14 CH$_2$); 0.81 (t, $J = 6.94$ Hz, 6H, 2 CH$_3$). ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): $\delta = 173.3$ (C$=$O); 165.2 (N$=$CH); 167.1; 165.2; 161.6; 144.2; 133.0; 122.8 (quaternary arom. C); 130.8; 128.6; 122.6; 115.0 (arom. C); 68.4 (CH$_2$O); 34.4 (O$_2$CC$\underline{\text{H}}_2$); 31.9; 29.6; 29.2; 26.0; 22.7 (aliph. C); 14.1 (2 CH$_3$). IR (KBr disk): cm$^{-1} = 1740$ (C$=$O); 3030 (Csp^2–H); 2923 (Csp^3–H); 1613 (C$=$C).

3c, with $R = n$-C$_9$H$_{19}$. ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): $\delta = 8.88$ (s, 1H, N$=$C$\underline{\text{H}}$); 7.97 (d, $J = 8.65$ Hz, 2H, arom. H); 7.85 (d, $J = 8.85$ Hz, 2H, arom. H) 7.19 (d, $J = 8.61$ Hz, 2H, arom. H); 6.93 (d, $J = 8.88$ Hz, 2H, arom. H); 3.95 (t, $J = 6.53$ Hz, 2H, OC$\underline{\text{H}}_2$); 2.52 (t, $J = 6.49$ Hz, 2H, O$_2$CC$\underline{\text{H}}_2$); 1.22 (m, 30H, 15 CH$_2$); 0.86 (t, $J = 6.64$ Hz, 6H, 2 CH$_3$). ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): $\delta = 173.5$ (C$=$O); 171.7 (N$=$CH); 166.9; 165.2; 161.6; 144.7; 132.6; 123.0 (quaternary arom. C); 131.5; 129.5; 122.4; 115.1 (arom. C); 68.3 (CH$_2$O); 34.4 (CO$_2\underline{\text{C}}$H$_2$); 31.4; 29.4; 29.3; 26.0; 24.8; 22.6 (aliph. C); 14.1 (2 CH$_3$). IR (KBr disk): cm$^{-1} = 1747$ (C$=$O); 3030 (Csp^2–H); 2923 (Csp^3–H); 1571 (C$=$C).

4.4. *n-Alkyl-4-formylbenzoates (**4a–c**)*

These compounds were synthesized using the same procedure as described for series **3a–c**. Products in liquid form were obtained which were used in subsequent reactions without further purification. The following yields of the crude products were obtained : **4a** 56%, **4b** 55%, **4c** 56%.

4a, $R = n$-C$_8$H$_{17}$. ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): $\delta = 9.89$ (s, 1H, O$=$C$\underline{\text{H}}$); 7.58 (d, $J = 8.13$ Hz, 2H, arom. H); 7.35 (d, $J = 8.10$ Hz, 2H, arom. H); 3.74 (t, $J = 6.67$ Hz, 2H, CO$_2$C$\underline{\text{H}}_2$); 1.09 (m, 12H, 6 CH$_2$); 0.22 (t, $J = 6.66$ Hz, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): $\delta = 191.3$ (O$=\underline{\text{C}}$H); 165.4 (C$=$O); 139.1; 136.4 (quaternary arom. C); 131.2; 129.1 (arom. C); 64.8 (CO$_2\underline{\text{C}}$H$_2$); 31.8; 29.5; 29.2; 28.6; 25.7; 22.5 (aliph. C); 13.8 (CH$_3$). IR (film): cm$^{-1} = 1718$ (C$=$O); 2927 (Csp^3–H); 1462 (C$=$C).

4b, $R = n$-C$_9$H$_{19}$. ^{1}H NMR (CDCl$_3$, TMS, 250 MHz): $\delta = 8.84$ (s, 1H, O$=$C$\underline{\text{H}}$); 7.57 (d, $J = 8.10$ Hz, 2H, arom. H); 7.33 (d, $J = 8.06$ Hz, 2H, arom. H); 3.75 (t, $J = 6.63$ Hz, 2H, CO$_2$C$\underline{\text{H}}_2$); 1.05 (m, 14H, 7 CH$_2$); 0.24 (t, $J = 6.68$ Hz, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, TMS, 62.9 MHz): $\delta = 190.9$ (O$=\underline{\text{C}}$H); 165.0 (C$=$O); 139.2; 136.5 (quaternary arom. C); 131.3; 129.0; (arom. C); 64.8 (CO$_2\underline{\text{C}}$H$_2$); 32.7; 31.8; 29.4; 29.2; 28.5; 25.7; 22.6 (aliph. C); 14.0 (CH$_3$). IR (film): cm$^{-1} = 1718$ (C$=$O); 2927 (Csp^3–H); 1462 (C$=$C).

4c, $R = n$-C$_{10}$H$_{21}$. ^{1}H NMR (CDCl$_3$, TMS,

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250 MHz): $\delta = 9.86$ (s, 1H, O=C$\underline{H}$); 7.59 (d, $J = 8.15$ Hz, 2H, arom. H); 7.34 (d, $J = 8.00$ Hz, 2H, arom. H); 3.73 (t, $J = 6.64$ Hz, 2H, $CO_2C\underline{H_2}$); 1.02 (m, 16H, 8 CH_2); 0.25 (t, $J = 6.70$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): $\delta = 191.5$ (O=$\underline{C}$H); 165.5 (C=O); 139.0; 135.4 (quaternary arom. C); 130.0; 129.3; (arom. C); 65.6 ($CO_2\underline{C}H_2$); 32.7; 31.8; 29.4; 28.5; 25.9; 26.7; 22.6 (aliph. C); 14.0 (CH_3). IR (film): $cm^{-1} = 1716$ (C=O); 2926 (Csp^3–H); 1461 (C=C).

4.5. *n-Alkyl 4-{[5-(4-n-decyloxyphenyl-1,3,4-thiadiazol-2-yl)imino]methyl}benzoates (**5a–c**)*

These compounds were synthesized by condensation of aminothiadiazole **1** with compounds of series **4a–c** using the same procedure as described for Schiff's bases **2**. The following yields were obtained: **5a** 44%, **5b** 38%, **5c** 38%.

5a, $R = n\text{-}C_8H_{17}$. ^1H NMR ($CDCl_3$, TMS, 250 MHz): $\delta = 9.02$ (s, 1H, N=C$\underline{H}$); 8.08 (d, $J = 8.42$ Hz, 2H, arom. H); 7.98 (d, $J = 8.48$ Hz, 2H, arom. H); 7.85 (d, $J = 8.83$ Hz, 2H, arom. H); 6.94 (d, $J = 8.91$ Hz, 2H, arom.H); 4.28 (t, $J = 6.68$ Hz, 2H, $CO_2C\underline{H_2}$); 3.95 (t, $J = 6.56$ Hz, 2H, $OC\underline{H_2}$); 1.21 (m, 28H, 14 CH_2); 0.81 (t, $J = 7.10$ Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): $\delta = 172.3$ (C=O); 165.2 (N=CH); 167.9; 165.8; 161.7; 138.1; 134.3; 122.7 (quaternary arom. C); 130.1; 129.9; 129.2; 115.0 (arom. C); 68.3 (CH_2O); 65.7 ($CO_2\underline{C}H_2$); 31.9; 31.8; 29.8; 29.5; 29.3; 29.2; 28.6; 26.0; 22.7 (aliph. C); 14.1 (2 CH_3). IR (KBr disk): $cm^{-1} = 1709$ (C=O); 3025 (Csp^2–H); 2921 (Csp^3–H); 1612 (C=C).

5b, $R = n\text{-}C_9H_{19}$. ^1H NMR ($CDCl_3$, TMS, 250 MHz): $\delta = 9.02$ (s, 1H, N=C$\underline{H}$); 8.19 (d, $J = 8.41$ Hz, 2H, arom. H); 8.08 (d, $J = 8.46$ Hz, 2H, arom. H); 7.92 (d, $J = 8.80$ Hz, 2H, arom. H); 6.99 (d, $J = 8.88$ Hz, 2H, arom.H); 4.35 (t, $J = 6.68$ Hz, 2H, $CO_2C\underline{H_2}$); 4.02 (t, $J = 6.56$ Hz, 2H, $OC\underline{H_2}$); 1.27 (m, 30H, 15 CH_2); 0.87 (t, $J = 6.91$ Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): $\delta = 172.3$ (C=O); 165.2 (N=CH); 167.8; 165.8; 161.7; 138.2; 134.4; 122.7 (quaternary arom. C); 130.0; 129.9; 129.2; 115.0 (arom. C); 68.3 (CH_2O); 65.7 ($CO_2\underline{C}H_2$); 31.9; 29.5; 29.3; 29.1; 28.6; 26.0; 22.7 (aliph. C); 14.1 (2 CH_3). IR (KBr disk): $cm^{-1} = 1710$ (C=O); 3020 (Csp^2–H); 2922 (Csp^3–H); 1611 (C=C).

5c, $R = n\text{-}C_{10}H_{21}$. ^1H NMR ($CDCl_3$, TMS, 250 MHz): $\delta = 8.96$ (s, 1H, N=C$\underline{H}$); 8.18 (d, $J = 8.40$ Hz, 2H, arom. H); 8.08 (d, $J = 8.43$ Hz, 2H, arom. H); 7.93 (d, $J = 8.82$ Hz, 2H, arom. H); 7.00 (d, $J = 8.85$ Hz, 2H, arom.H); 4.28 (t, 6.63 Hz, 2H, $CO_2C\underline{H_2}$); 4.01 (t, $J = 6.58$ Hz, 2H, $OC\underline{H_2}$); 1.27 (m, 32H, 16 CH_2); 0.85 (t, $J = 6.60$ Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): $\delta = 172.3$ (C=O); 165.8 (N=CH); 167.8; 165.2; 161.7; 138.2; 134.4; 122.8 (quaternary arom. C); 130.1; 129.9; 129.3; 115.1 (arom. C); 68.3 (CH_2O); 65.7 ($CO_2\underline{C}H_2$); 31.9; 29.5; 29.3; 26.0; 22.7 (aliph. C); 14.1 (2 CH_3). IR (KBr disk): $cm^{-1} = 1710$ (C=O); 3030 (Csp^2–H); 2920 (Csp^3–H); 1610 (C=C).

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