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Symmetric esters derived from 1,3,4-oxadiazole: synthesis, mesomorphic properties and structural study by semi-empirical calculations

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Three homologous series of symmetric esters derived from 2-alkylthio-5-(*p*-hydroxy)phenyl-1,3,4-oxadiazole (series **3**, **4** and **5**) were synthesized and their liquid crystalline properties investigated by optical microscopy and differential scanning calorimetry. Depending on the chain length, nematic and smectic C phases were observed in the series **3**; smectic A and smectic C phases in series **4**. None of the homologues of series **5** shows mesomorphic properties. These three series are compared with other previously reported oxadiazoles. A structural study of AM1 semi-empirical calculations is also described.

1. Introduction

Mesomorphic compounds containing heterocyclic units have previously been synthesized and interest in such structures constantly grows. This is not only because of the greater possibilities with heterocyclic rings for the design of new mesogenic molecules, but also because the introduction of heteroatoms can cause considerable changes in polarity, polarizability and geometry of the molecules [1–4]. These can greatly influence the types of mesophases which occur, their phase transitions temperatures, and the dielectric and other properties of the mesogens [5, 6].

Heterocyclic compounds such as five-membered thiadiazole or thiophene rings can be incorporated into the principal structure of calamitic mesogens [7–12]. In contrast to this, compounds with an oxygen atom in an aromatic ring are rare. 1,3,4-Oxadiazole derivatives were first described by Dimitrowa *et al.*, with the oxadiazole ring in the central position. But comparison of these compounds with the analogous thiadiazole derivatives reveals that the replacement of sulphur by oxygen causes a complete loss of liquid crystalline properties [5]. The same results were obtained with the thiadiazoles and oxadiazoles previously reported by us [12]. Nevertheless, mesogenic oxadiazole derivatives have been synthesized [12–20] and patents describing some examples of liquid crystalline oxadiazole derivatives have been published [21–24].

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Previously, we reported a homologous series of symmetric esters derived from 2-alkylthio-5-(*p*-hydroxy)-phenyl-1,3,4-oxadiazole and *trans*-1,4,-cyclohexane-dicarboxylic acid (series **6**) [15]. In continuation of our investigations [15, 16, 20] on 2,5-disubstituted-1,3,4-oxadiazole derivatives, we have synthesized three new homologues series of symmetric esters (series **3**, **4** and **5**), and have studied their thermodynamic and optical properties and structure/mesomorphic activity relationships.

2. Synthesis

The route adopted for the synthesis of the series **3**, **4** and **5** compounds is given in the scheme. The homologues series of diesters were synthesized by using 4-hydroxy-phenylhydrazide as precursor. The treatment of this with carbon disulfide in basic medium produces the thione **1**. In the following sequence, the selective S-alkylation of **1** leads to the homologues series of oxadiazoles **2**, according to the procedure reported in references [14, 15]. By esterification of **2** with the corresponding carboxylic acid chloride, the homologues series of diesters (series **3**, **4** and **5**) were obtained.

3. Results and discussion

3.1. *Mesomorphic properties*

All compounds in the series **3a–f** display broad enantiotropic mesophase regions. The short chain derivatives ($n = 5, 6$) exhibit SmC–N dimorphism, the remaining members studied ($n = 7$–10) are purely SmC in character.

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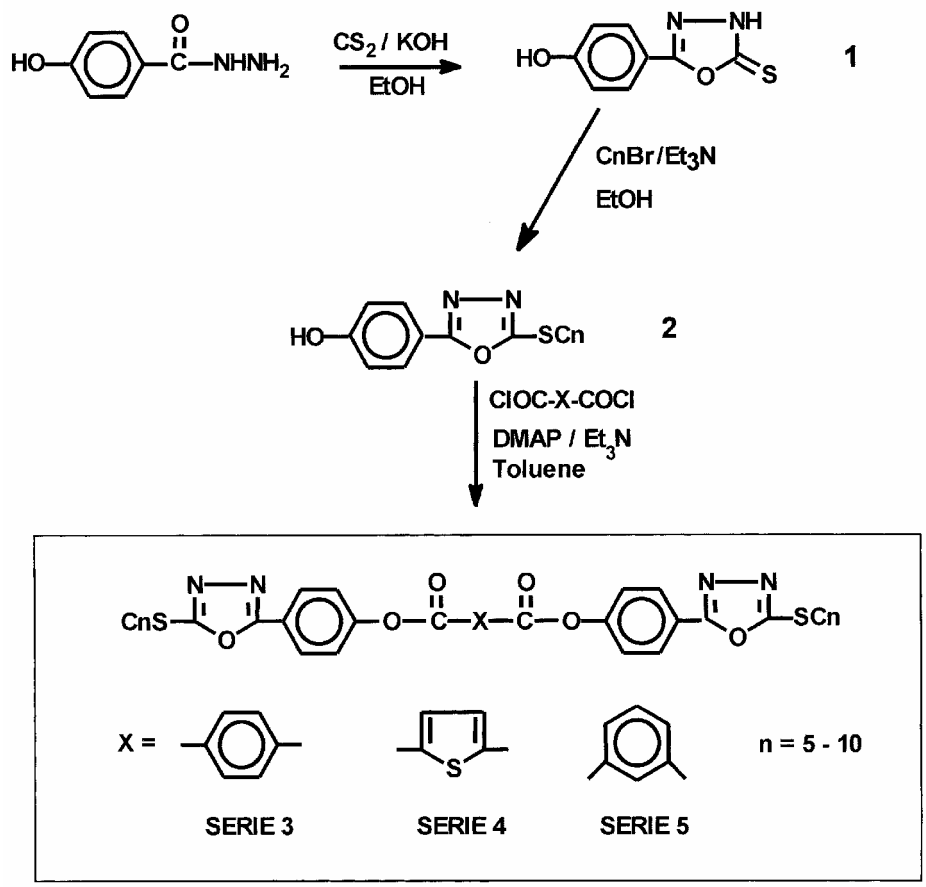

Scheme. Synthetic route for esters of series **3**, **4** and **5**.

In series **4a–f** the first two homologues ($n = 5, 6$) display an enantiotropic SmC phase, while the higher homologues ($n = 7$–10) exhibit SmC–SmA enantiotropic dimorphism. Compounds of the series **3a–f** have a lower melting point and a higher clearing temperature than the compounds of the series **4a–f**; i.e. the homologues of the series **3** have higher thermal stability and broader mesomorphic range.

The optical, thermal and thermodynamic data for the compounds of series **3** and **4** are gathered in tables 1 and 2. A graphical representation of the mesomorphic behaviour as a function of the number (n) of carbon atoms in the lateral chain is presented in figures 1 and 2. None of the compounds in series **5a–f** shows mesomorphic behaviour; only crystal–isotropic transitions (Cr–I) are observed.

The unique difference between these series is their central aromatic ring. The esters of series **3** are derived from terephthalic acid (*para*-substitution). The esters of series **4** are derived from 2,5-thiophene dicarboxylic acid and the esters of the series **5** are derived from isophthalic acid (*meta*-substitution). Clearly, the central aromatic ring and the positions of their substitutions, play an important role in the mesomorphic properties.

Table 1. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for series **3** compounds: Cr = crystal, SmC = smectic C, N = nematic, I = isotropic.

Compound	Transition	Temperature	ΔH
3a ($n = 5$)	Cr–SmC	129	37.1
	SmC–N	279	1.5
	N–I	292	0.6
3b ($n = 6$)	Cr–SmC	134	48.7
	SmC–N	278	1.7
	N–I	283	0.8
3c ($n = 7$)	Cr–SmC	116	21.6
	SmC–I	281	5.5
3d ($n = 8$)	Cr–SmC	116	49.4
	SmC–I	275	10.2
3e ($n = 9$)	Cr–SmC	113	44.3
	SmC–I	268	8.1
3f ($n = 10$)	Cr–SmC	110	33.2
	SmC–I	244	10.4

These results and the thermal data presented in tables 1 and 2 show that the introduction of the benzene ring, with *para*-substitution, into the molecular core of series **3**

Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) for series **4** compounds: Cr = crystal, SmC = smectic C, SmA = smectic A, I = isotropic.

Compound	Transition	Temperature	ΔH
4a ($n = 5$)	Cr–SmC	143	27.7
	SmC–I	228	5.8
4b ($n = 6$)	Cr–SmC	136	23.7
	SmC–I	226	6.5
4c ($n = 7$)	Cr–SmC	136	25.2
	SmC–SmA	215[a]	—
	SmA–I	225	7.5
4d ($n = 8$)	Cr–SmC	131	25.1
	SmC–SmA	203[a]	—
	SmA–I	224	8.2
4e ($n = 9$)	Cr–SmC	130	26.3
	SmC–SmA	212[a]	—
	SmA–I	220	8.5
4f ($n = 10$)	Cr–SmC	127	29.7
	SmC–SmA	215[a]	—
	SmA–I	219	9.4

[a] Optical microscopy data.

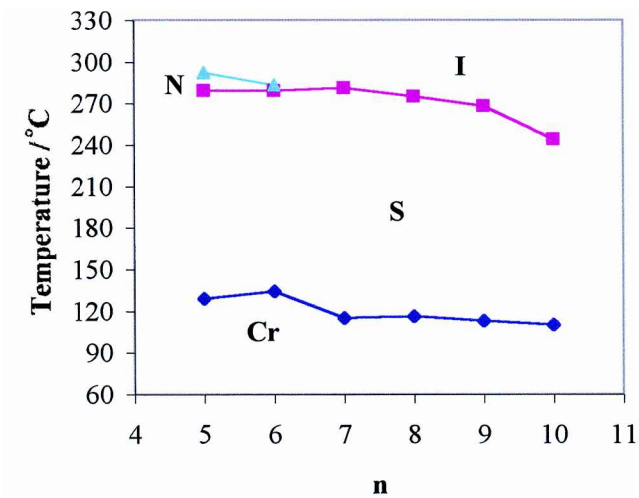

Figure 1. Plot of transition temperatures versus the number of carbon atoms (n) in the thioalkyl chain for series **3** compounds.

produces liquid crystals with a lower melting point and higher clearing temperature than the compounds of the series **4**, in which the central aromatic ring comprises a thiophene heterocyclic. Probably, the thiophene ring in series **4** should lead to deviation from the typical rod-like mesogen symmetry, explaining the lower mesomorphic range compared with compounds of series **3**. On the other hand, replacement of the *para*-substituted benzene ring (series **3**) or thiophene heterocyclic (series **4**) by a benzene ring with *meta*-substitution results in the disappearance of the mesophase in the compounds of series **5**, indicating that in these compounds the deviation

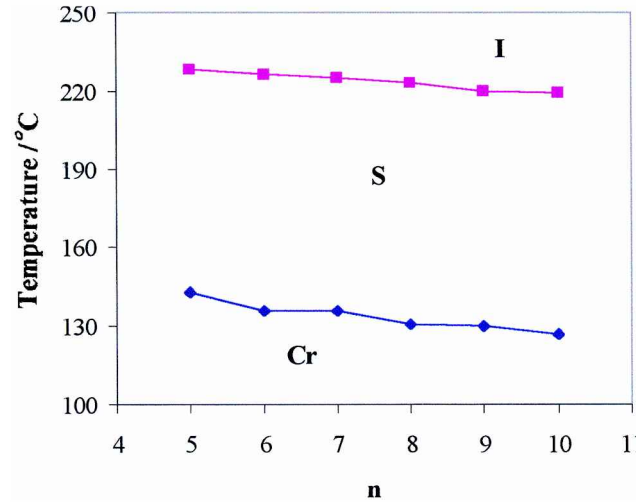

Figure 2. The plot of transition temperatures versus the number of carbon atoms (n) in the thioalkyl chain for series **4** compounds.

from typical rod-like mesogen symmetry is much more pronounced, leading to a complete loss of liquid crystalline properties.

Cai and Samulski [4] studied non-linear molecular shape effects in symmetric *para*-substituted phenyl esters of 2,5-thiophene dicarboxylic acid and similar analogues of isophthalic acid, which have an exocyclic bond angle of 148° and 120°, respectively. They also reported that while ester homologues derived from 2,5-thiophene dicarboxylic acid were mesomorphic, the analogues derived from isophthalic acid did not exhibit liquid crystallinity—the same mesomorphic behaviour that we have obtained with the compounds of series **4** and **5**. From these results we assume that the oxadiazoles derived from 2,5-thiophene dicarboxylic acid reported in this paper (series **4**) are more linear than the similar analogues of oxadiazoles derived from isophthalic acid (series **5**).

We have also compared the esters of series **3** with the homologues of the esters derived from *trans*-1,4,-cyclohexane dicarboxylic acid, previously reported by us [15] (series **6**, figure 3) which have the following mesomorphic properties (temperatures in °C):

$n = 5$ Cr 161.1 SmC 243.5 N 265.0 I
$n = 6$ Cr 146.6 SmC 243.5 N 250.0 I
$n = 7$ Cr 144.1 SmC—244.4 I
$n = 8$ Cr 137.4 SmC—239.4 I
$n = 9$ Cr 142.0 SmC—235.0 I
$n = 10$ Cr 139.5 SmC—240.0 I.

Series **3** and **6** display the same mesophases; in both series the homologues with $n = 5, 6$ exhibit dimorphism SmC–N, and in the higher homologues ($n = 7$–10) only the SmC phase is observed. However, series **3** has a

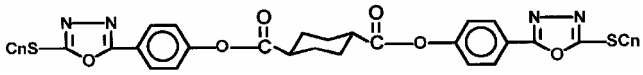

Figure 3. Structure of series **6** compounds.

greater mesomorphic range than series **6**. This could be explained by considering the central ring: in series **3** this is benzene, whereas in series **6** it is a cyclohexane ring (*trans*-1,4-disubstituted). Probably, the high thermal stability of series **3** compounds is due to the aromatic ring giving rise to a more planar structure, allowing for stronger molecular interactions in the liquid crystalline phase.

It is also interesting to compare the mesogenic properties of these esters (series **3**, **4** and **6**) with esters reported by Dingemans *et al.* [17] (ODBP-PH-O-C12 in figure 4). The more important difference is the position occupied by the oxadiazole ring in the rigid core. In series synthesized here, the oxadiazole ring occupies the terminal position of the rigid aromatic core, and this heterocyclic may be looked upon as a polar terminal substituent. In contrast to this, in the Dingemans esters the oxadiazole ring is in the central part of the aromatic rigid core which has a non-linear boomerang shape. This difference has some effect on the liquid crystalline properties. First, the compounds of series **3** have higher transition temperatures and broader mesomorphic ranges than those reported for ODBP-PH-O-C12. The same results are observed in series **6**, but in this case the mesomorphic range is similar to that of ODBP-PH-O-C12 (~100°C). Second, the homologues of series **4** show higher melting and clearing temperatures and lower mesomorphic ranges than those of ODBP-PH-O-C12 (~90°C).

3.2. *Textures observed by polarizing optical microscopy*

The mesophases exhibited by series **3** and **4** compounds were identified according to their optical textures which were observed by optical microscopy both on heating and on cooling. The SmC mesophase exhibited by series **3** esters was identified by the appearance of a broken focal-conic texture coexisting with the fine four-brush schlieren texture. The N phase of these compounds showed the characteristic marble texture and the typical schlieren texture with two- and four-brush singularities. Esters of series **4** showed the typical bâtonnet texture, coalescing to form a fan-shaped texture. Mechanical stress leads to the formation of a homeotropic texture.

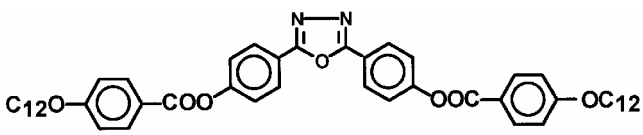

Figure 4. Structure of ODBP-PH-OC12.

The texture observed for the SmC phase was schlieren with only two-brush singularities.

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 [25, 26]. We used the derivatives with a thiomethyl terminal chain as molecular model and explored the potential energy hypersurface. Several initial conformations were optimized, for the three series of compounds (**3**, **4** and **5**). In general, no great difference of energy was found between the different conformations generated from the relative disposition of the heterocyclic rings and carboxylic groups. In all cases, the difference of energy between the different conformations is less than 0.5 kcal mol^{-1}. For the three series (**3**, **4** and **5**) those conformations with the carbonyl group *anti* with respect to the central ring were the most stable.

However, the linearity of the compounds is affected by the relative orientation of the carboxylic group. Thus, as expected, there is a gradual loss of linearity from series **3** to series **5**. Figure 5 shows the two extreme conformations denoted *syn* and *anti*. In series **5** there is a great loss of linearity. For the series **4**, with a central thiophene ring, the *syn* conformation is not linear, while in series **3** both conformations maintain linearity. These facts are responsible for the great stability of the mesomorphic phase in series **3** compounds with respect to the other two series; the loss of mesomorphism in series **5** is also explained.

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 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 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-Hydroxy)phenyl-3H-1,3,4-oxadiazoline-2-thione (**1**)*

This compound was synthesized by the method described in references [14, 15].

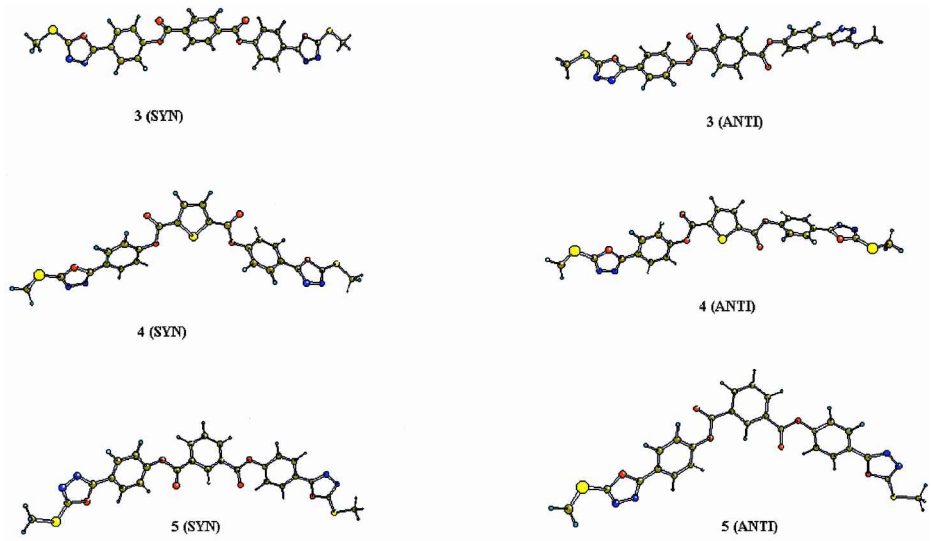

Figure 5. Diagram of the *syn*- and *anti*-conformations of esters **3**, **4** and **5**.

4.2. *2-n-Alkylthio-5-(4-hydroxy)phenyl-1,3,4-oxadiazoles (**2**)*

These compounds were synthesized by the method described in references [14, 15].

4.3. *Bis[4-(5-n-alkylthio-1,3,4-oxadiazole-2-yl)phenyl terephthaloate (**3a–f**)*

The general method of references [15] was used. To a solution of 3.13 mmole of **2**, 0.032 g of 4-dimethylaminopyridine (DMAP) and 1 ml of triethylamine in 35 ml of dry toluene, was added 1.56 mmole (0.33 g) of terephthaloyl dichloride, previously synthesized. The mixture was stirred overnight at room temperature. The precipitate formed was filtered off and purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (7/3) as eluent, and then recrystallized twice from ethanol/toluene (4/1). Yields were 20, 16, 12, 19, 10 and 21% for compounds **3a**, **3b**, **3c**, **3d**, **3e** and **3f**, respectively.

3a. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.39 (s, 4H, H of the central benzene ring); 8.14 (d, J = 8.67 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 7.45 (d, J = 8.66 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 3.37 (t, J = 7.31 Hz, 4H, 2 SCH_2); 1.92–1.33 (m, 12H, 6 CH_2); 0.90 (t, J = 6.60 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 170.2 (C=O); 164.8; 164.6; 153.1; 133.6; 121.7 (quaternary arom. C); 130.4; 128.0; 122.3 (arom. C); 32.6; 29.2; 28.5; 22.5; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 1725 (C=O); 3074 (Csp^2–H); 2930 (Csp^3–H); 1600 (C=C).

3b. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.40 (s, 4H, H of the central benzene ring); 8.16 (d, J = 8.80 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 7.44 (d, J = 8.79 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 3.32 (t, J = 7.31 Hz, 4H, 2 SCH_2); 1.93–1.33 (m, 16H, 8 CH_2); 0.92 (t, J = 6.80 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS 62.9 MHz): δ ppm = 169.8 (C=O); 163.9; 163.5; 153.1; 133.7; 121.8 (quaternary arom. C); 130.4; 128.1; 122.4 (arom. C); 32.7; 31.7; 29.0; 28.6; 22.6; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 1725 (C=O); 3071 (Csp^2–H); 2928 (Csp^3–H); 1600 (C=C).

3c. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.39 (s, 4H, H of the central benzene ring); 8.14 (d, J = 8.75 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 7.45 (d, J = 8.73 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 3.37 (t, J = 7.32 Hz, 4H, 2 SCH_2); 1.94–1.30 (m, 20H, 10 CH_2); 0.91 (t, J = 6.73 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS 62.9 MHz): δ ppm = 169.9 (C=O); 164.6; 163.8; 153.2; 133.9; 121.8 (quaternary arom. C); 130.3; 128.0; 121.9 (arom. C); 32.7; 31.7; 29.2; 29.0; 28.6; 22.5; 13.9 (aliph. C). IR (KBr disk): cm^{-1} = 1722 (C=O); 3070 (Csp^2–H); 2929 (Csp^3–H); 1600 (C=C).

3d. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.41 (s, 4H, H of the central benzene ring); 8.20 (d, J = 8.68 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 7.44 (d, J = 8.70 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 3.34 (t, J = 7.31 Hz, 4H, 2 SCH_2); 1.90–1.32 (m, 24H, 12 CH_2); 0.93 (t, J = 6.69 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS 62.9 MHz): δ ppm = 170.0 (C=O); 164.9; 163.6; 153.2; 133.8; 122.0 (quaternary arom. C); 130.3; 127.9; 121.6 (arom. C); 31.9; 31.7; 30.2; 28.6; 24.6; 14.2 (aliph. C). IR (KBr disk): cm^{-1} = 1725 (C=O); 3071 (Csp^2–H); 2931 (Csp^3–H); 1600 (C=C).

3e. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.40 (s, 4H, H of the central benzene ring); 8.16 (d, J = 8.70 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 7.45 (d, J = 8.72 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 3.38 (t, J = 7.32 Hz, 4H, 2 SCH_2); 1.94–1.31 (m, 28H, 14 CH_2); 0.92 (t, J = 6.70 Hz, 6H,

2 CH_3). ^{13}C NMR ($CDCl_3$, TMS 62.9 MHz): δ ppm = 169.8 (C=O); 164.8; 163.7; 153.1; 133.7; 121.7 (quaternary arom. C); 130.4; 128.1; 121.7 (arom. C); 32.7; 31.7; 29.2; 28.6; 22.6; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 1725 (C=O); 3074 (Csp^2–H); 2931 (Csp^3–H); 1600 (C=C).

3f. ^1H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.39 (s, 4H, H of the central benzene ring); 8.15 (d, J = 8.71 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 7.46 (d, J = 8.72 Hz, 4H, H of two benzene rings joined to oxadiazole rings); 3.38 (t, J = 7.33 Hz, 4H, 2 SCH_2); 1.92–1.33 (m, 32H, 16 CH_2); 0.90 (t, J = 6.68 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS 62.9 MHz): δ ppm = 170.2 (C=O); 165.0; 163.6; 153.2; 133.9; 122.0 (quaternary arom. C); 130.5; 128.0; 121.8 (arom. C); 33.0; 32.7; 30.2; 29.0; 28.6; 22.6; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 1724 (C=O); 3068 (Csp^2–H); 2930 (Csp^3–H); 1600 (C=C).

4.4. *Bis[4-(5-n-alkylthio-1,3,4-oxadiazole-2-yl)phenyl 2,5-thiophenedicarboxylate (**4a–f**)*

The method of synthesis was similar to that given for compounds **3a–f**. Yields were 70, 70, 75, 75, 70 and 60% for compounds **4a**, **4b**, **4c**, **4d**, **4e** and **4f**, respectively.

4a. ^1H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.10 (d, J = 2.48 Hz, 4H, benzene rings); 7.99 (s, 2H, thiophene ring); 7.40 (d, J = 2.47 Hz, 4H, benzene rings); 3.29 (t, J = 7.29 Hz, 4H, 2 SCH_2); 1.89–1.21 (m, 12H, 6 CH_2); 0.88 (t, 6.30 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 165.0 (C=O); 164.5; 159.0; 152.8; 139.2; 122.0 (quaternary arom. C); 135.0 (CH, thiophene ring); 128.0; 122.1 (CH, benzene rings); 32.5; 29.9; 28.9; 23.0; 14.2 (aliph. C). IR (KBr disk): cm^{-1} = 1727 (C=O); 3100 (Csp^2–H); 2930 (Csp^3–H); 1605 (C=C).

4b. ^1H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.12 (d, J = 2.49 Hz, 4H, benzene rings); 8.10 (s, 2H, thiophene ring); 7.36 (d, J = 2.48 Hz, 4H, benzene rings); 3.29 (t, J = 7.27 Hz, 4H, 2 SCH_2); 1.89–1.21 (m, 16H, 8 CH_2); 0.90 (t, 6.30 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 165.0 (C=O); 164.7; 159.0; 152.7; 139.3; 122.0 (quaternary arom. C); 134.8 (CH, thiophene ring); 128.2; 122.3 (CH, benzene rings); 33.1; 31.7; 29.4; 29.0; 22.6; 14.1 (aliph. C). IR (KBr disk): cm^{-1} = 1726 (C=O); 3102 (Csp^2–H); 2934 (Csp^3–H); 1605 (C=C).

4c. ^1H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.11 (d, J = 2.49 Hz, 4H, benzene rings); 7.99 (s, 2H, thiophene ring); 7.39 (d, J = 2.48 Hz, 4H, benzene rings); 3.31 (t, J = 7.30 Hz, 4H, 2 SCH_2); 1.91–1.19 (m, 20H, 10 CH_2); 0.89 (t, 6.28 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 164.8 (C=O); 164.6; 158.9; 153.0; 139.3; 122.0 (quaternary arom. C); 134.9 (CH, thiophene ring); 128.0; 122.0 (CH, benzene rings); 33.7; 32.7; 30.5; 29.4; 29.0; 22.6; 14.1 (aliph. C). IR (KBr disk): cm^{-1} = 1724 (C=O); 3104 (Csp^2–H); 2933 (Csp^3–H); 1606 (C=C).

4d. ^1H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.05 (d, J = 2.46 Hz, 4H, benzene rings); 8.01 (s, 2H, thiophene ring); 7.39 (d, J = 2.45 Hz, 4H, benzene rings); 3.31 (t, J = 7.30 Hz, 4H, 2 SCH_2); 1.89–1.20 (m, 24H, 12 CH_2); 0.86 (t, 6.32 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 165.0 (C=O); 164.7; 159.1; 152.8; 139.2; 122.0 (quaternary arom. C); 134.8 (CH, thiophene ring); 128.1; 122.4 (CH, benzene rings); 32.6; 31.9; 29.4; 29.2; 29.1; 28.7; 22.8; 14.3 (aliph. C). IR (KBr disk): cm^{-1} = 1726 (C=O); 3100 (Csp^2–H); 2932 (Csp^3–H); 1606 (C=C).

4e. ^1H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.06 (d, J = 2.46 Hz, 4H, benzene rings); 8.01 (s, 2H, thiophene ring); 7.39 (d, J = 2.47 Hz, 4H, benzene rings); 3.31 (t, J = 7.29 Hz, 4H, 2 SCH_2); 1.89–1.19 (m, 28H, 14 CH_2); 0.90 (t, 6.32 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 165.0 (C=O); 164.7; 159.2; 152.7; 139.3; 121.9 (quaternary arom. C); 134.8 (CH, thiophene ring); 128.0; 122.1 (CH, benzene rings); 32.8; 31.7; 29.4; 29.3; 29.0; 28.8; 22.7; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 1725 (C=O); 3102 (Csp^2–H); 2932 (Csp^3–H); 1607 (C=C).

4f. ^1H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.07 (d, J = 2.47 Hz, 4H, benzene rings); 8.00 (s, 2H, thiophene ring); 7.38 (d, J = 2.48 Hz, 4H, benzene rings); 3.30 (t, J = 7.28 Hz, 4H, 2 SCH_2); 1.90–1.20 (m, 32H, 16 CH_2); 0.87 (t, 6.33 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 164.9 (C=O); 164.8; 159.2; 152.6; 139.4; 121.9 (quaternary arom. C); 134.7 (CH, thiophene ring); 128.1; 122.2 (CH, benzene rings); 32.7; 31.8; 29.5; 29.4; 29.2; 29.0; 28.6; 22.6; 14.1 (aliph. C). IR (KBr disk): cm^{-1} = 1726 (C=O); 3102 (Csp^2–H); 2933 (Csp^3–H); 1607 (C=C).

4.5. *Bis[4-(5-n-alkylthio-1,3,4-oxadiazole-2-yl)phenyl isophthaloate (**5a–f**)*

The method of synthesis procedure was similar to that given for compounds **3a–f**. Yields were 54, 55, 60, 69, 74 and 50% for compounds **5a**, **5b**, **5c**, **5d**, **5e** and **5f**, respectively. Melting points (°C) were 140, 150, 158, 154, 150 and 159, respectively.

5a. ^1H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 9.00 (s, 1H, central benzene ring); 8.39 (d, J = 1.78 Hz; 2H, central benzene ring); 8.10 (d, J = 1.97 Hz, 4H, benzene rings joined to oxadiazole rings); 7.71 (t, J = 7.84 Hz, 1H, central benzene ring); 7.39 (d, J = 1.96 Hz, 4H, benzene rings joined to oxadiazole rings); 3.30 (t, J = 7.28 Hz, 4H, 2 SCH_2); 1.82–1.43 (m, 12H, 6 CH_2); 0.90 (t, J = 6.40 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 165.0 (C=O); 164.6; 163.7; 152.9; 129.1; 121.8 (quaternary arom. C); 135.0; 131.8; 130.0 (central benzene ring); 128.4; 122.3 (benzene rings joined to oxadiazole

rings); 32.8; 30.3; 28.8; 22.5; 14.2 (aliph. C). IR (KBr disk): cm^{-1} = 1725 (C=O); 3100 (Csp^2–H); 2927 (Csp^3–H); 1602 (C=C).

5b. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 9.01 (s, 1H, central benzene ring); 8.45 (d, J = 1.77 Hz; 2H, central benzene ring); 8.10 (d, J = 1.99 Hz, 4H, benzene rings joined to oxadiazole rings); 7.69 (t, J = 7.83 Hz, 1H, central benzene ring); 7.40 (d, J = 1.98 Hz, 4H, benzene rings joined to oxadiazole rings); 3.30 (t, J = 7.30 Hz, 4H, 2 SCH_2); 1.88–1.43 (m, 16H, 8 CH_2); 0.88 (t, J = 6.40 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 165.1 (C=O); 164.8; 163.6; 153.2; 129.2; 122.0 (quaternary arom. C); 135.0; 133.0; 129.9 (central benzene ring); 128.2; 122.3 (benzene rings joined to oxadiazole rings); 32.7; 31.8; 30.0; 28.8; 22.5; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 1727 (C=O); 3098 (Csp^2–H); 2930 (Csp^3–H); 1600 (C=C).

5c. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.98 (s, 1H, central benzene ring); 8.50 (d, J = 1.77 Hz; 2H, central benzene ring); 8.10 (d, J = 1.97 Hz, 4H, benzene rings joined to oxadiazole rings); 7.68 (t, J = 7.82 Hz, 1H, central benzene ring); 7.40 (d, J = 1.96 Hz, 4H, benzene rings joined to oxadiazole rings); 3.28 (t, J = 7.30 Hz, 4H, 2 SCH_2); 1.80–1.39 (m, 20H, 10 CH_2); 0.90 (t, J = 6.37 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 164.8 (C=O); 164.5; 163.5; 152.9; 129.2; 121.8 (quaternary arom. C); 135.1; 132.0; 129.7 (central benzene ring); 128.1; 122.2 (benzene rings joined to oxadiazole rings); 32.8; 32.0; 29.1; 29.0; 28.6; 22.8; 14.3 (aliph. C). IR (KBr disk): cm^{-1} = 1725 (C=O); 3098 (Csp^2–H); 2929 (Csp^3–H); 1602 (C=C).

5d. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 9.00 (s, 1H, central benzene ring); 8.47 (d, J = 1.77 Hz; 2H, central benzene ring); 8.10 (d, J = 1.98 Hz, 4H, benzene rings joined to oxadiazole rings); 7.72 (t, J = 7.87 Hz, 1H, central benzene ring); 7.40 (d, J = 1.97 Hz, 4H, benzene rings joined to oxadiazole rings); 3.30 (t, J = 7.29 Hz, 4H, 2 SCH_2); 1.88–1.39 (m, 24H, 12 CH_2); 0.90 (t, J = 6.40 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 165.1 (C=O); 164.8; 163.7; 153.2; 129.4; 121.8 (quaternary arom. C); 135.4; 132.0; 130.0 (central benzene ring); 128.3; 122.6 (benzene rings joined to oxadiazole rings); 32.8; 31.8; 29.4; 29.1; 28.9; 28.6; 22.4; 14.1 (aliph. C). IR (KBr disk): cm^{-1} = 1725 (C=O); 3099 (Csp^2–H); 2930 (Csp^3–H); 1600 (C=C).

5e. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.99 (s, 1H, central benzene ring); 8.44 (d, J = 1.76 Hz; 2H, central benzene ring); 8.06 (d, J = 1.99 Hz, 4H, benzene rings joined to oxadiazole rings); 7.70 (t, J = 7.85 Hz, 1H, central benzene ring); 7.38 (d, J = 1.95 Hz, 4H, benzene rings joined to oxadiazole rings); 3.29 (t, J = 7.28 Hz, 4H, 2 SCH_2); 1.80–1.40 (m, 28H, 14 CH_2); 0.86 (t, J = 6.38 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 164.9 (C=O); 164.7; 163.5; 153.0; 129.3; 121.6 (quaternary arom. C); 135.2; 131.8; 129.9 (central benzene ring); 128.0; 122.4 (benzene rings joined to oxadiazole rings); 32.6; 31.7; 29.3; 29.2; 29.1; 28.9; 28.5; 22.5; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 1725 (C=O); 3099 (Csp^2–H); 2929 (Csp^3–H); 1602 (C=C).

5f. ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ ppm = 8.98 (s, 1H, central benzene ring); 8.46 (d, J = 1.78 Hz; 2H, central benzene ring); 8.10 (d, J = 1.98 Hz, 4H, benzene rings joined to oxadiazole rings); 7.71 (t, J = 7.86 Hz, 1H, central benzene ring); 7.39 (d, J = 1.97 Hz, 4H, benzene rings joined to oxadiazole rings); 3.30 (t, J = 7.30 Hz, 4H, 2 SCH_2); 1.83–1.39 (m, 32H, 16 CH_2); 0.90 (t, J = 6.41 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δ ppm = 164.8 (C=O); 164.7; 163.7; 152.9; 129.5; 122.1 (quaternary arom. C); 135.3; 132.0; 130.0 (central benzene ring); 128.2; 122.5 (benzene rings joined to oxadiazole rings); 33.6; 32.4; 31.9; 30.3; 29.5; 29.3; 28.9; 28.2; 22.7; 14.0 (aliph. C). IR (KBr disk): cm^{-1} = 1726 (C=O); 3098 (Csp^2–H); 2930 (Csp^3–H); 1602 (C=C).

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