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Microwave-assisted synthesis and liquid crystal properties of 1,3,4-thiadiazole-based liquid crystals

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A series of 2-(4-alkoxyphenyl)-5-*p*-tolyl-1,3,4-thiadiazole derivatives **2a**–**2h** were synthesised efficiently under microwave irradiation and solvent-free conditions. The thermal properties were determined using polarised optical microscopy (POM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). All these compounds exhibited enantiotropic liquid crystal properties with wide mesomorphic temperature ranges and good thermal stability. Compounds **2a**–**2f** with short alkoxy chain (n = 1–6) all exhibited an enantiotropic nematic mesophase, while both nematic and smectic C mesophases were observed in compounds **2g** (n = 7) and **2h** (n = 8) with longer alkoxy spacer. The effect of the length of the alkoxy chain on liquid crystal properties is discussed in this paper.

Keywords: microwave-assisted synthesis; 1,3,4-thiadiazole; odd–even effect; liquid crystals

1. Introduction

Since Zaschke first reported the mesogenic 2,5-diphenyl-1,3,4-oxadiazole/1,3,4-thiadiazole derivatives (*1*), there has been a continuing interest in liquid crystal materials derived from these structural motifs due to the rich mesophases and the potential application in liquid crystal display materials and electronic devices such as light-emitting diodes and photovoltaic cells (for reviews see (*2*,*3*), for selected papers see (*4*–*5*)). Up to now, quite a lot of mesogenic 1,3,4-oxadiazoles with various molecular shapes have been studied by different research groups (for rod-like mesogens, see (*6*–*10*); for disk-like mesogens, see (*11*,*12*), for star-like mesogens (*13*)). In contrast, the corresponding 1,3,4-thiadiazole analogues are relatively less reported in the literature, although the heterocyclic 1,3,4-thiadizole is regarded as being more favourable to form mesophases with wide mesomorphic temperature ranges (*14*–*17*). From the synthetic point, the 1,3,4-oxadiazole-based compounds can be synthesised successfully by several methods (*18*), while the approaches to preparing the 1,3,4-thiadiazoles are limited. The formation of the 1,3,4-thiadiazole ring is usually carried out by sulphuration of the *N,N′*-diacylhydrazines using reagents such as P_4S_{10} (*19*) and Lawesson's reagent (*20*–*22*) in anhydrous hydrocarbon solvent at elevated temperatures. These conventional methods often suffer drawbacks such as low to moderate yields, long reaction times, and many byproducts. Recently, Kiryanov *et al.* (*23*) and other research groups (*24*,*25*) reported the synthesis of thiadiazoles and other sulphur-based heterocycles using microwave irradiation as a non-conventional energy source, which was proven to be an efficient approach with many advantages such as short reaction times, solvent-free conditions, low costs, and simple work-up. However, the examples of 1,3,4-thiadiazole-based compounds synthesised by microwave irradiation were relatively scarce, and few of them are mesogenic compounds (*26*).

In this study, a series of 2-(4-alkoxyphenyl)-5-*p*-tolyl-1,3,4-thiadiazoles **2a**–**2h** were synthesised in high yields under microwave irradiation and solvent-free conditions. All of these compounds have the same 2,5-diphenyl-1,3,4-thiadiazole unit connected with an alkoxy chain and a terminal methyl group. The reason for the selection of methyl as the terminal group is that the mesogenic 1,3,4-thiadiazole derivatives with this group often exhibit richer mesophases and wider mesomorphic temperature ranges than the analogues with other groups (*27*) Furthermore, compounds with end methyl group can be structurally modified easily to prepare various liquid crystal materials. The structures and purity of the products **2a**–**2h** were characterised by IR, ^{1}H-NMR, MS, and elemental analysis. All of these compounds exhibited stable liquid crystal behaviours in a wide temperature range; the effect of the alkoxy chain on the nature of the mesophases and the mesomophic temperature ranges were investigated. Notably, compound **2a** is the mesogenic 1,3,4-thiadiazole derivative with the shortest alkyl (CH_3) and alkoxy (CH_3O) chains.

2. Results and discussion

2.1 Synthesis

The synthetic route with reaction conditions is shown in Scheme 1. The products **2a**–**2h** were prepared under

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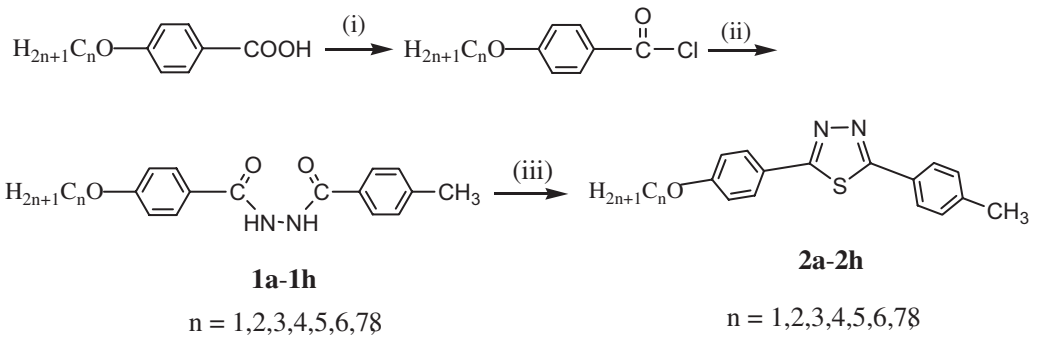

Scheme 1. The synthetic route to compounds **2a**–**2h**. Reagents and conditions: (i) $SOCl_2$, toluene, reflux, 7 h; (ii) Pyridine, 4-methylbenzhydrazide, 60°C, 2 h; (iii) Microwave irradiation, Lawesson's reagent.

microwave irradiation and solvent-free conditions in a common household microwave oven. The total reaction time for each product is only 120∼130 seconds, the whole work-up process is simple and clean, and this preparative method could be conveniently carried out in a gram scale in good yields (80–91%), which are greatly improved in contrast to the method using the conventional energy source. The key factor for this reaction is to control the irradiation time precisely. The microwave irradiation should be stopped immediately the reaction mixture has turned into liquid as prolonged irradiation will result in side products – even the combustion of the reaction mixture.

2.2 Mesomorphic properties

The liquid crystal behaviors of the compounds **2a**–**2h** were investigated by polarising optical microscopy (POM), differential scanning calorimetry (DSC) and thermogravimetric analysis. The mesophases were identified according to their optical textures using the classification systems reported by Kumar (*28*) and Dierking (*29*). The phase transitions and the associated enthalpy are summarised in Table 1.

As seen in Table 1, compounds **2a**–**2f** with shorter terminal chain (n = 1–6) only exhibited an enantiotropic nematic phase, which was assigned from the typical schlieren or thread-like textures as seen in Figure 1(a) and Figure 1(b), respectively. With increasing the length of the alkoxy chain (n = 7, 8), the corresponding compounds **2g** and **2h** displayed both nematic and smectic C mesophases. The smectic C phase was identified by the Schlieren texture (Figure 1(c)), which was observed upon cooling from the nematic phase with marbled and thread-like texture (Figure 1(d)). The mesophases assignments according to the POM observations are in good

Table 1. Phase transition temperatures and enthalpies for **2a**–**2h**: measured at a heating/cooling rate of 5°C min^{-1} under a 20 ml min^{-1} flow of argon.

Compound	Transition[a]	T (°C)	ΔH (kJ mol^{-1})
2a	Cr → N	152.6	27.7
	N → Iso	215.5	0.7
	Iso → N	214.2	–0.9
	N → Cr	137.9	–23.8
2b	Cr → N	140.7	25.3
	N → Iso	223.3	1.2
	Iso → N	222.2	–1.2
	N → Cr	120.0	–14.9
2c	Cr → N	145.0	31.4
	N → Iso	200.0	0.9
	Iso → N	199.3	–0.7
	N → Cr	120.0	–28.3
2d	Cr → N	135.6	22.3
	N → I	198.7	0.6
	I → N	197.7	–0.6
	N → Cr	104.0	–18.0
2e	Cr → N	121.8	24.0
	N → I	190.2	0.7
	I → N	189.5	–0.7
	N → Cr	99.5	–22.0
2f	Cr →N	113.7	17.8
	N →I	189.5	0.9
	I →N	188.6	–1.0
	N →Cr	89.4	–18.2
2g	Cr → SmC	110.3	10.6
	SmC → N	115.5	5.5
	N → I	185.1	0.7
	I → N	184.2	–0.7
	N → SmC	116.6	–0.5
	SmC → Cr	94.5	–17.9
2h	Cr → SmC	105.9	21.3
	SmC → N	124.6	0.4
	N → I	183.8	0.7
	I → N	182.8	–0.7
	N → SmC	123.4	–0.4
	SmC → Cr	85.5	–17.8

[a]Cr, crystalline; N, nematic; SmC, smectic C; Iso, isotropic phase.

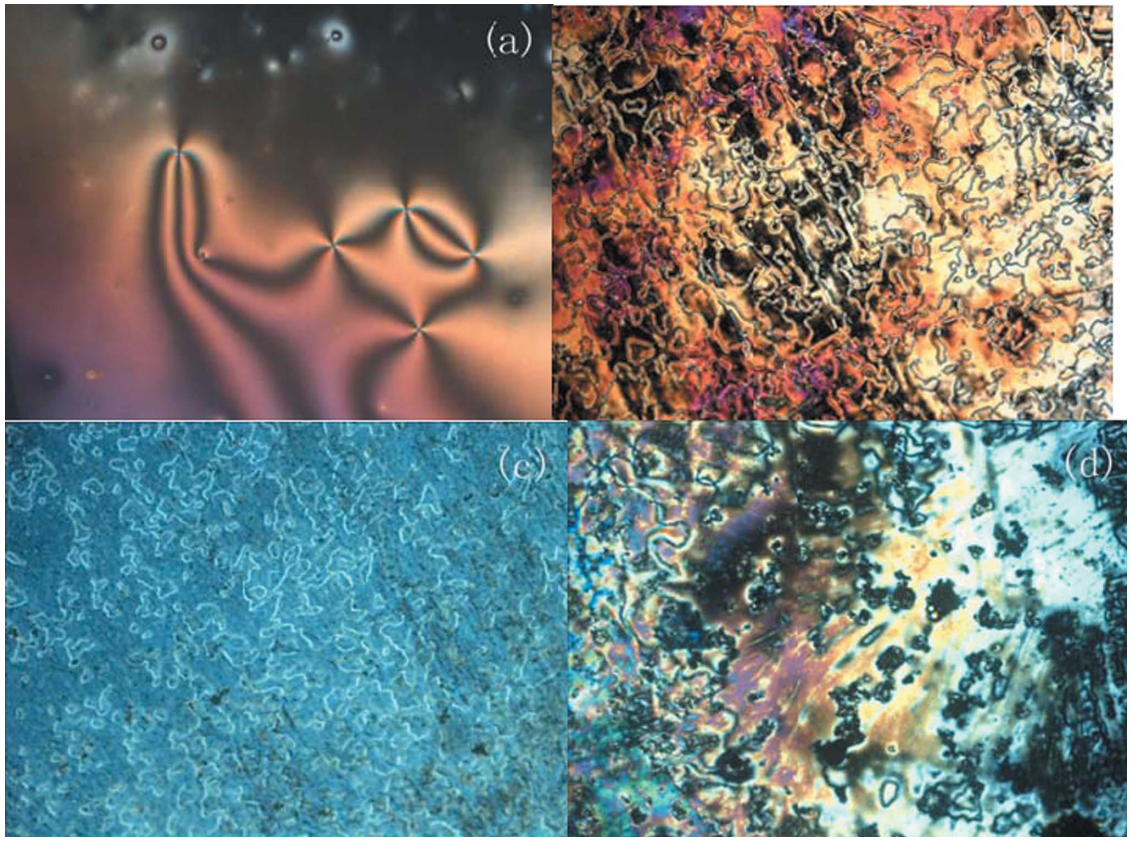

Figure 1. Optical micrographs (magnification: ×200) of (a) the nematic schlieren texture observed for **2a**, at 218°C on heating cycle; (b) the nematic thread-like texture observed for **2c**, at 181°C on cooling cycle; (c) the schlieren smectic C texture of **2h** at 123.3°C on cooling cycle; (d) the thread-like texture of **2h** at 186°C on heating cycle.

agreement with the corresponding DSC thermograms. All of the compounds **2a**–**2h** exhibit clear-cut transition temperatures in their DSC thermograms. As a representative example, Figure 2 depicts the DSC thermograms of compound **2h**. On the first heating scans, the DSC curve of **2h** showed three endothermic peaks at 105.9, 124.6, and 183.8°C, which were assigned to the crystal-to-SmC, SmC-to-nematic and nematic-to-isotropic liquid transitions, respectively. Upon cooling, there were three exothermic peaks that were attributed to the isotropic to nematic at 182.8°C, nematic to SmC at 123.4 and SmC to solid transition at 85.5°C, respectively.

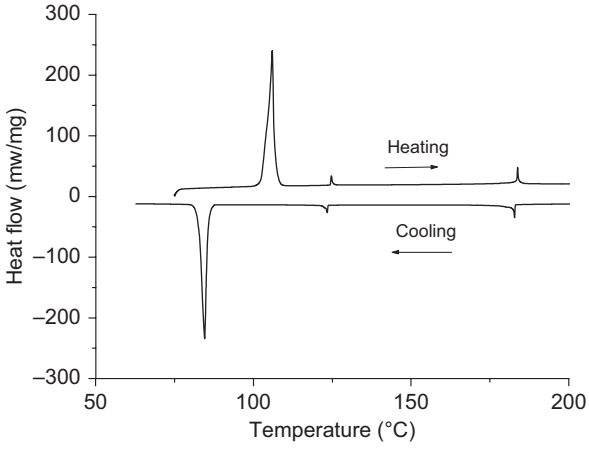

Figure 2. The differential scanning calorimetry thermograms, **2h**.

2.3 The effect on the length of the alkoxy chain on the liquid crystalline properties

Figure 3 shows the transition temperatures versus the number of carbon atoms in the alkoxy chain for **2a**–**2h** in the heating cycle. It is clear that the length of the alkoxy chain influenced not only the nature of the mesophases but also the mesomorphic temperature ranges. Generally, an increase in terminal length often results in an enhanced induced-dipole–induced-dipole interaction between the terminal chains, leading to the formation of more ordered smectic mesophase in rod-like mesogens. Consequently, compounds **2g** and **2h** exhibited a smectic C phase as well as a nematic

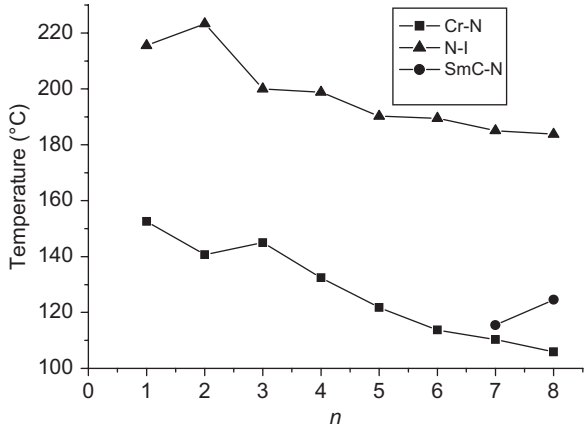

Figure 3. Plot of transition temperatures versus the number of carbon atoms (*n*) in the alkoxy chain for **2a**–**2h**.

phase, while the other analogues only displayed a nematic phase due to the shorter alkoxy chain. As seen in Figure 3, both the melting and clearing temperature points of **2a**–**2h** tend to decrease with increasing alkoxy chain length, and the clearing temperature points are in good accordance with the odd–even alternation. It's worthy to note that compound **2a** is the mesogenic 1,3,4-thiadiazole compound with the shortest alkoxy and alkyl chains.

2.4 The thermogravimetric analysis

Since these substituted 1,3,4-thiadiazole derivatives are chemically reminiscent of each other, the thermal stabilities of compounds **2d**, **2f, 2g** and **2h** were selected to investigate by thermogravimetric analysis (TGA). Figure 4 depicts the TGA curves of the solid samples of **2d**, **2f, 2g** and **2h**, which were recorded at 25–400°C under N_2 atmosphere. It can be seen that all these

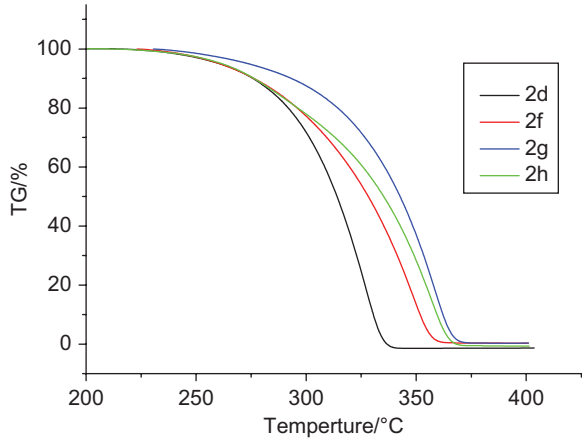

Figure 4. The thermogravimetric analysis curves for **2d**, **2f, 2g** and **2h.**

compounds decomposed by a one-step process and showed different onset decomposition temperatures (*Td*) (327°C for **2d**, 348°C for **2f**, 358°C for **2g**, 357°C for **2h**). The decomposition temperatures increase with the elongation of the alkoxy chain and are much higher than those of the 1,3,4-oxadiazole-based compounds, which decomposed by a two-step process *(9)*. The results show that the 1,3,4-thiadiazole-based liquid crystals possess much better thermal stability than the corresponding 1,3,4-oxadiazole analogues. It's noted that all the solid samples showed insignificant weight losses in the temperature range 25–240°C, indicative of absence of solvent of crystallisation, which is consistent with the results of the DSC thermograms and the elemental analysis data.

3. Conclusions

A series of aromatically substituted 1,3,4-thiadiazoles **2a**–**2h** have been synthesised in good yields under microwave irradiation and solvent-free conditions. All of the final products exhibit enantiotropic liquid crystalline behaviours with good thermal stability. The results showed that:

(1) Compounds **2a**–**2f** with short alkoxy chain exhibit only nematic mesophase, with increasing the length of the terminal alkoxy chain. An additional smectic C phase was observed in **2g** and **2h**.
(2) The odd–even alternation in clearing points was observed in this series of compounds.
(3) Compound **2a** was found to be the mesogenic thiadiazole compound with the shortest flexible chains.

4. Experimental

4.1 General

IR spectra were recorded in KBr discs with a Bio-RadFTS 6000 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AV300 spectrometer using $CDCl_3$ as solvent and TMS as the internal standard. Elemental analyses were carried out using a Yanaco CHN CORDER MT-3 apparatus. ESI-MS were obtained on a Finnigan LCQ Advantage. Mesophase textures were studied using a polarising optical microscope (OLYMPUS BX51) equipped with a hot stage. Transition temperatures and enthalpies of the final compounds were determined by differential scanning calorimetry (Q100 V9.0 Build 275) with heating and cooling rates of 10°C ·min^{-1}.

p-alkoxy-substituted benzoic acids were prepared according to the literature *(30)*. All the other chemicals and solvents were analytical grades and obtained

from commercial sources. The microwave-assisted reactions were carried out using a commercial conventional microwave oven (Glanz WP800TL23-K1).

4.2. Synthesis

*4.2.1 Synthesis of 4-methylbenzoic acid N′-(4-alkoxy benzoyl)hydrazide **1a–1d***

To a round bottomed flask (100 ml) was added toluic acid (0.02 mol), thionyl chloride (3 ml) and anhydrous toluene (20 ml) and the resultant mixture was refluxed for 7 h under nitrogen. Then the excess thionyl chloride was removed under reduced pressure, to the residue was added *p*-alkoxybenzoyl hydrazide (0.02 mol) and pyridine (15 ml), and the resultant mixture was heated for 2 h at 50–60°C and stirred at room temperature overnight. Then the reaction mixture was poured in distilled water (50 ml) to give the crude products as light yellow solids, which were purified by recrystallisation from ethanol twice to give the products as white solids.

4-methylbenzoic acid N′-(4-methoxybenzoyl) hydrazide **1a**: White solids, yield 85%. ^{1}H NMR (300MHz, $CDCl_3$) δ: 2.41 (s, 3H, Ar-CH_3), 3.86 (s, 3H, CH_3O-), 6.94 (d, 2H, J = 8.7 Hz, Ar-H), 7.26 (d, 2H, J = 7.8 Hz, Ar-H), 7.76 (d, 2H, J = 7.8 Hz, Ar-H), 7.84 (d, 2H, J = 8.7 Hz, Ar-H), 9.31 (s, 2H, N-H). MS-ESI (%): 283.35 ($(M-1)^-$, 100).

4-methylbenzoic acid N′-(4-ethoxybenzoyl)hydrazide **1b**: White solids, yield 87%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.44 (t, 3H, J = 6.9 Hz, **CH_3**CH_2O -), 2.40 (s, 3H, Ar-CH_3), 4.08 (q, 2H, J = 6.6 Hz, -CH_2O-), 6.90 (d, 2H, J = 9.0 Hz, Ar-H), 7.24 (d, 2H, J = 8.1 Hz, Ar-H), 7.75 (d, 2H, J = 8.1 Hz, Ar-H), 7.82 (d, 2H, J = 9.0 Hz, Ar-H), 9.41 (d, 1H, J = 6.0 Hz, N-H), 9.44 (d, 1H, J = 6.0 Hz, N-H). MS-ESI (%): 297.35 ($(M-1)^-$, 100).

4-methylbenzoic acid N′-(4-propoxybenzoyl)hydrazide **1c**: White solids, yield 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.05 (t, 3H, J = 6.9 Hz, **CH_3**CH_2CH_2O -), 1.83 (sext, 2H, CH_3**CH_2**CH_2O -), 2.41 (s, 3H, Ar-CH_3), 3.97 (t, 2H, J = 6.6 Hz, -CH_2O-), 6.93 (d, 2H, J = 8.4 Hz, Ar-H), 7.26 (d, 2H, J = 8.0 Hz, Ar-H), 7.76 (d, 2H, J = 8.0 Hz, Ar-H), 7.82 (d, 2H, J = 7.6 Hz, Ar-H), 9.30 (d, 1H, J = 6.0 Hz, N-H), 9.34 (d, 1H, J = 6.0 Hz, N-H). MS-ESI (%): 311.28 ($(M-1)^-$, 100).

4-methylbenzoic acid N′-(4-butylbenzoyl) hydrazide **1d**: White solids, yield 72.2%. m.p. 187–189°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.99 (t, 3H, J = 7.4 Hz, **CH_3**CH_2-), 1.52 (sext, 2H, CH_3C**H_2**-), 1.78 (quint, 2H, -C**H_2**CH_2O-), 2.41 (s, 3H, Ar-CH_3), 4.01 (t, 2H, J = 6.5 Hz, -CH_2O-), 6.93 (d, 2H, J = 8.8 Hz, Ar-H), 7.27 (d, 2H, J = 8.1 Hz, Ar-H), 7.76 (d, 2H, J = 8.1 Hz, Ar-H), 7.82 (d, 2H, J = 8.8 Hz, Ar-H), 9.22 (d, 1H, J = 6.0 Hz, N-H), 9.26 (d, 1H, J = 6.0 Hz, N-H).

4-methylbenzoic acid N′-(4-pentylbenzoyl)hydrazide **1e**: White solids, yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, 3H, J = 6.9 Hz, **CH_3**CH_2-), 1.24–1.45 (m, 4H, $CH_3(C$**H_2**$)_2CH_2CH_2O$-), 1.74 (quint, 2H, -C**H_2**CH_2O-), 2.33 (s, 3H, Ar-CH_3), 3.92 (t, 2H, J = 6.5 Hz, -CH_2O-), 6.83 (d, 2H, J = 8.7 Hz, Ar-H), 7.16 (d, 2H, J = 8.1 Hz, Ar-H), 7.69 (d, 2H, J = 7.8 Hz, Ar-H), 7.75 (d, 2H, J = 8.7 Hz, Ar-H), 9.36 (d, 1H, J = 6.0 Hz, N-H), 9.39 (d, 1H, J = 6.0 Hz, N-H).

4-methylbenzoic acid N′-(4-hexylbenzoyl)hydrazide **1f**: White solids, yield 81.6%. m.p. 179–181°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, 3H, J = 6.4Hz, **CH_3**CH_2-), 1.34-1.49 (m, 6H, $CH_3(C$**H_2**$)_3CH_2CH_2O$-), 1.80 (quint, 2H, -C**H_2**CH_2O-), 2.41 (s, 3H, Ar-CH_3), 4.00 (t, 2H, J = 6.5 Hz, -CH_2O-), 6.91 (d, 2H, J = 8.6 Hz, Ar-H), 7.25 (d, 2H, J = 7.9 Hz, Ar-H), 7.76 (d, 2H, J = 7.9 Hz, Ar-H), 7.82 (d, 2H, J = 8.6 Hz, Ar-H), 9.41 (d, 1H, J = 6.0 Hz, N-H), 9.45 (d, 1H, J = 6.0 Hz, N-H).

4-methylbenzoic acid N′-(4-heptylbenzoyl)hydrazide **1g**: White solids, yield 79.5%. m.p. 168–170°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, 3H, J = 6.8 Hz, **CH_3**CH_2-), 1.31–1.48 (m, 8H, $CH_3(C$**H_2**$)_4CH_2CH_2O$-), 1.80 (quint, 2H, -C**H_2**CH_2O-), 2.41 (s, 3H, Ar-CH_3), 4.00 (t, 2H, J = 6.6 Hz, -CH_2O-), 6.94 (d, 2H, J = 8.4 Hz, Ar-H), 7.27 (d, 2H, J = 8.2 Hz, Ar-H), 7.76 (d, 2H, J = 7.9 Hz, Ar-H), 7.82 (d, 2H, J = 8.5 Hz, Ar-H), 9.23 (d, 1H, J = 6.0 Hz, N-H), 9.26 (d, 1H, J = 6.0 Hz, N-H).

4-methylbenzoic acid N′-(4-octylbenzoyl)hydrazide **1h**: White solids, yield 83.7%. m.p. 158–160°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, 3H, J = 6.6 Hz, **CH_3**CH_2-), 1.29-1.45 (m, 10H, $CH_3(C$**H_2**$)_5CH_2CH_2O$-), 1.80 (quint, 2H, -C**H_2**CH_2O-), 2.40 (s, 3H, Ar-CH_3), 3.99 (t, 2H, J = 6.6 Hz, -CH_2O-), 6.90 (d, 2H, J = 8.8 Hz, Ar-H), 7.23 (d, 2H, J = 8.4 Hz, Ar-H), 7.76 (d, 2H, J = 8.0 Hz, Ar-H), 7.82 (d, 2H, J = 8.7 Hz, Ar-H), 9.49 (d, 1H, J = 6.0 Hz, N-H), 9.54 (d, 1H, J = 6.0 Hz, N-H).

4.2.2 Synthesis of 2-(4-alkoxylphenyl)-5-p-tolyl-1, 3, 4-thiadiazoles 2a–2h

One of the intermediate compounds **1a–1h** (0.76 mmol) and Lawesson's reagent [2,4-Bis-(4-methoxyphenyl)-, 3-dithia-2,4-diphosphetane 2,4-disulphide] (310 mg, 0.76 mol) were mixed thoroughly and placed in a 10-ml glass test tube. The tube was placed in a beaker and irradiated in a household microwave oven (Glanz WP800TL23-K1, 800W) for about 120–130 seconds. When the mixture became a liquid, the reaction was deemed to be finished and the irradiation was immediately stopped to prevent degradation of the product. The tube was removed from the oven after the reaction mixture cooled down. The crude product dissolved in chloroform and was purified to obtain the corresponding products **2a–2h** by silica gel column

chromatography using ethyl acetate/dichloromethane (1:25) as eluent.

2-(4-methoxyphenyl)-5-*p*-tolyl-1,3,4-thiadiazole **2a**: White solids, yield 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.42 (s, 3H, Ar-CH_3), 3.88 (s, 3H, CH_3O-), 7.00 (d, 2H, J = 8.8 Hz, Ar-H), 7.29 (d, 2H, J = 8.0 Hz, Ar-H), 7.89 (d, 2H, J = 8.0 Hz, Ar-H), 7.95 (d, 2H, J = 8.8 Hz, Ar-H). MS-ESI (%): 283.28 ($(M+1)^+$, 100). Elemental analysis: calculated for $C_{16}H_{14}N_2OS$: C 68.06, H 5.0, N 9.92; found C 68.14, H 5.17, N 10.13.

2-(4-ethoxyphenyl)-5-*p*-tolyl-1,3,4-thiadiazole **2b**: White solids, yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.46 (t, 3H, J = 6.9 Hz, **CH_3**CH_2O-), 2.43 (s, 3H, Ar-CH_3), 4.11 (q, 2H, J = 6.9 Hz, -CH_2O-), 6.99 (d, 2H, J = 8.4 Hz, Ar-H), 7.29 (d, 2H, J = 7.8 Hz, Ar-H), 7.89 (d, 2H, J = 8.4 Hz, Ar-H), 7.95 (d, 2H, J = 8.8 Hz, Ar-H). MS-ESI (%): 297.36 ($(M+1)^+$, 100). Elemental analysis: calculated for $C_{17}H_{16}N_2OS$: C 68.89, H 5.44, N 9.45; found C 69.10, H 5.24, N 9.52.

2-(4-propoxyphenyl)-5-*p*-tolyl-1,3,4-thiadiazole **2c**: White solids, yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.06 (t, 3H, J = 6.6 Hz, **CH_3**CH_2CH_2O -), 1.85 (quint, 2H, CH_3**CH_2**CH_2O -), 2.43 (s, 3H, Ar-CH_3), 4.00 (t, 2H, J = 6.6 Hz, -CH_2O-), 6.99 (d, 2H, J = 8.8 Hz, Ar-H), 7.30 (d, 2H, J = 7.6 Hz, Ar-H), 7.76 (d, 2H, J = 8.0 Hz, Ar-H), 7.82 (d, 2H, J = 7.6 Hz, Ar-H). MS-ESI (%): 311.29 ($(M+1)^+$, 100). Elemental analysis: calculated for $C_{18}H_{18}N_2OS$: C 69.65, H 5.84, N 9.02; found C 69.75, H 5.78, N 8.89.

2-(4-butyloxyphenyl)-5-*p*-tolyl-1,3,4-thiadiazole **2d**: White solids, yield, 91.6%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.00 (t, 3H, J = 6.6 Hz, **CH_3**CH_2-), 1.56 (sext, 2H, CH_3**CH_2**-), 1.81 (quint, 2H, -**CH_2**CH_2O-), 2.44 (s, 3H, Ar-CH_3), 4.05 (t, 2H, J = 6.5 Hz, -CH_2O-), 7.02 (d, 2H, J = 8.1 Hz, Ar-H), 7.32(d, 2H, J = 7.9 Hz, Ar-H), 7.93 (d, 2H, J = 7.9 Hz, Ar-H), 8.04 (d, 2H, J = 7.9 Hz, Ar-H); IR (KBr) ν: 2938, 2864, 1603, 1517, 1444, 1257, 1179, 836, 819, 725cm^{-1}; MS (relative intensity %): m/z: 325 (M^++1, 16), 324 (M^+, 73); elemental analysis: calculated for $C_{19}H_{20}N_2OS$: C 70.34, H 6.21, N 8.63; found C 70.22, H 6.18, N 8.72.

2-(4-pentyloxyphenyl)-5-*p*-tolyl-1,3,4-thiadiazole **2e**: White solids, yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.95 (t, 3H, J = 6.6 Hz, **CH_3**CH_2-), 1.34–1.52 (m, 4H, CH_3(**CH_2**)$_2CH_2CH_2O$-), 1.81 (quint, 2H, -**CH_2**CH_2O-), 2.42 (s, 3H, Ar-CH_3), 4.02 (t, 2H, J = 6.5 Hz, -CH_2O-), 6.98 (d, 2H, J = 8.7 Hz, Ar-H), 7.29 (d, 2H, J = 8.1 Hz, Ar-H), 7.88 (d, 2H, J = 8.1 Hz, Ar-H), 7.93 (d, 2H, J = 8.7 Hz, Ar-H). MS (relative intensity %): m/z: 339 (M^++1, 100), 340 (M^++2, 30); elemental analysis: calculated for $C_{20}H_{22}N_2OS$: C 70.97, H 6.55, N 8.28; found C 71.06, H 6.18, N 8.06.

2-(4-hexyloxyphenyl)-5-*p*-tolyl-1,3,4-thiadiazole **2f**: White solids, yield 93.3%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.92 (t, 3H, J = 6.6 Hz, **CH_3**CH_2-), 1.34–1.51 (m, 6H, CH_3(**CH_2**)$_3CH_2CH_2O$-), 1.81 (quint, 2H, -**CH_2**CH_2O-), 2.43 (s, 3H, Ar-CH_3), 4.03 (t, 2H, J = 6.6 Hz, -CH_2O-), 6.99 (d, 2H, J = 8.8Hz, Ar-H), 7.30 (d, 2H, J = 8.1 Hz, Ar-H), 7.90(d, 2H, J = 8.1 Hz, Ar-H), 7.96 (d, 2H, J = 8.8 Hz, Ar-H); IR (KBr) ν: 2931, 2862, 1603, 1517, 1444, 1258, 1179, 836, 819, 725 cm^{-1}; MS (relative intensity %): m/z: 353 (M^++1, 13), 352 (M^+, 48); Elemental analysis: calculated for $C_{21}H_{24}N_2OS$: C 71.55, H 6.86, N 7.95; found C 71.63, H 6.97, N 7.89.

2-(4-heptyloxyphenyl)-5-*p*-tolyl-1,3,4-thiadiazole **2g**: White solids, yield 92.1%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, 3H, J = 6.5Hz, **CH_3**CH_2-), 1.32–1.52 (m, 8H, CH_3(**CH_2**)$_4CH_2CH_2O$-), 1.81 (quint, 2H, -**CH_2**CH_2O-), 2.43 (s, 3H, Ar-CH_3), 4.03 (t, 2H, J = 6.6 Hz, -CH_2O-), 6.99 (d, 2H, J = 8.7 Hz, Ar-H), 7.30 (d, 2H, J = 8.1 Hz, Ar-H), 7.89(d, 2H, J = 8.1 Hz, Ar-H), 7.95(d, 2H, J = 8.8 Hz, Ar-H); IR (KBr) ν: 2928, 2857, 1604, 1518, 1446, 1406, 1260, 1179, 835, 819, 723 cm^{-1}; MS (relative intensity %): m/z: 367 (M^++1, 12), 366 (M^+, 50); Elemental analysis: calculated for $C_{22}H_{26}N_2OS$: C 72.09, H 7.15, N 7.64; found C 71.23, H 7.30, N 7.50.

2-(4-octyloxyphenyl)-5-*p*-tolyl -1,3,4-thiadiazole **2h**: White solids, yield, 87.2%. ^{1}H NMR (300 MHz, $CDCl_3$) δ:0.89 (t, 3H, J = 6.7 Hz, **CH_3**CH_2-), 1.30–1.50 (m, 10H, CH_3(**CH_2**)$_5CH_2CH_2O$-), 1.83 (quint, 2H, -**CH_2**CH_2O-), 2.43 (s, 3H, Ar-CH_3), 4.03 (t, 2H, J = 6.5 Hz, -CH_2O-), 6.99 (d, 2H, J = 8.8 Hz, Ar-H), 7.30 (d, 2H, J = 8.0 Hz, Ar-H), 7.89 (d, 2H, J = 8.1 Hz, Ar-H), 7.94 (d, 2H, J = 8.8 Hz, Ar-H); IR (KBr) ν: 2921, 2856, 1604, 1518, 1445, 1406, 1260, 1179, 835, 819, 723 cm^{-1}; MS (relative intensity %): m/z: 381 (M^++1, 11), 380 (M^+, 38); Elemental analysis: calculated for $C_{23}H_{28}N_2OS$: C 72.59, H 7.42, N 7.36; found C 72.48, H 7.36, N 7.47.

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