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Alan M. Grubb[a]; Sana Hasan[a]; Andre A. Kiryanov; Paul Sampson[a]; Alexander J. Seed[a]
[a] Department of Chemistry, Kent State University, Kent, Ohio, USA

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The synthesis and physical evaluation of 5-alkoxy-1,3-thiazoles prepared via Lawesson's reagent-mediated cyclisation of α-benzamido esters

Alan M. Grubb[a], Sana Hasan, Andre A. Kiryanov[b], Paul Sampson[a] and Alexander J. Seed[a]*

[a]*Department of Chemistry, Kent State University, Kent, Ohio 44242-0001, USA;* [b]*Takeda San Diego, 10410, Science Center Drive, San Diego, CA 92921, USA*

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The synthesis of the first series of 5-alkoxy-1,3-thiazole-based liquid crystals is reported. The aforementioned liquid crystals were synthesised through a Lawesson's reagent-mediated cyclisation of appropriate α-benzamido esters. This methodology was found to be highly efficient, even on a large scale, and the resulting 5-alkoxy-1,3-thiazoles could be purified without the use of column chromatography. The synthesis and mesomorphic properties of a family of 5-alkoxy-2-(4-cyanophenyl)-1,3-thiazole liquid crystals prepared via this approach are discussed and compared with their thiophene and phenyl analogues.

Keywords: 1,3-thiazole; α-benzamido carbonyl; cyclisation

1. Introduction

The 1,3-thiazole ring has been incorporated into a variety of mesogenic structures and imparts a number of favourable physical properties including low viscosity (*1*) (anticipated due to the more compact nature of the ring compared with benzene), high birefringence, and a significant lateral dipole moment (1.6D) (*2*). In order to generate a relatively linear geometry, the 1,3-thiazole core may be either 2,5- or 2,4-disubstituted; the 2,5-disubstituted arrangement is the more linear substitution pattern (the angles defined by extrapolating the C–H bonds are 153.4° for 2,5-disubstitution and 132.8° for 2,4-disubstitution when the substituents are hydrogen for example (*2*)), which leads to enhanced mesophase thermal stability. The variety of substituents that have been incorporated into such structures is fairly limited and, for the 2,5-disubstituted-1,3-thiazoles includes 2,5-diphenyl (*3, 4*), 2-alkenyl-5-phenyl (*3*), 5-alkyl-2-phenyl (*3*), 2-alkyl-5-phenyl (*3*), 2,5-bisalkynyl (*5, 6*), 2-phenyl-5-thiazolo[5,4-*d*]thiazole (*7*), and 5-alkyl-2-benzylideneamino (*8*) moieties. For the 2,4-substitution pattern, substituents incorporated are limited to 4-phenyl-2-(1,3-thiazol-2-yl) (*3*), 4-(arylamino)-2-benzylideneamino- (*9–14*), and 2-benzylideneamino-4-(*p*-nitrophenoxy) (*13–15*). Fewer than 100 mesogenic 1,3-thiazoles have been reported in the open literature (LiqCryst database, version 4.6) and a number of additional structures have also been reported in the patent literature (*16–21*). A selection of representative examples is given in Figure 1.

We previously reported the first example of a liquid crystalline compound incorporating a 1,3-thiazole ring bearing an alkoxy substituent (*22*). The use of alkoxy side chains in liquid crystalline materials leads to increased mesophase thermal stability, higher polarisability, higher birefringence, and higher dielectric anisotropy when compared with analogous alkyl chains. Therefore, we embarked on a more extensive study of mesogens bearing a 5-alkoxythiazole moiety. In this paper, the synthesis of a series of novel 5-alkoxy-2-(4-cyanophenyl)-1,3-thiazoles is reported in order to evaluate the impact of the 5-alkoxy-1,3-thiazole core on mesogenic properties. We compared and contrasted the mesophase thermal stabilities with the analogous 2-alkoxy-5-(4-cyanophenyl)thiophenes and 4'-alkoxybiphenyl-4-ylcarbonitriles.

5-Alkoxy-1,3-thiazoles are most commonly synthesised through ring closure of an appropriately substituted α-acylamino carbonyl compound with either P_2S_5 or Lawesson's reagent (*23*). The use of P_2S_5 for the synthesis of 5-alkoxy-1,3-thiazoles has been well documented in mainstream organic chemistry but the yields vary greatly (44–88%) and the longest alkoxy chain investigated was only a propyloxy unit (*24–28*). Additionally, reactions using P_2S_5 for the synthesis of sulphur-based heterocycles have a tendency to be somewhat capricious (*29*). A search of the literature reveals that the use of Lawesson's reagent for the synthesis of 5-alkoxy-1,3-thiazoles has been less explored and only three groups have utilised this methodology. The seminal publication in this area involved the construction of 2-phenyl-5-ethoxy-1,3-thiazole from the appropriate α-acylamino carbonyl precursor in 85% yield (*30*). 5-Methoxy-2-pyridyl-1,3-thiazoles have also been prepared with yields ranging from 50% to 58% (2, 3 and

*Corresponding author. Email: aseed@kent.edu

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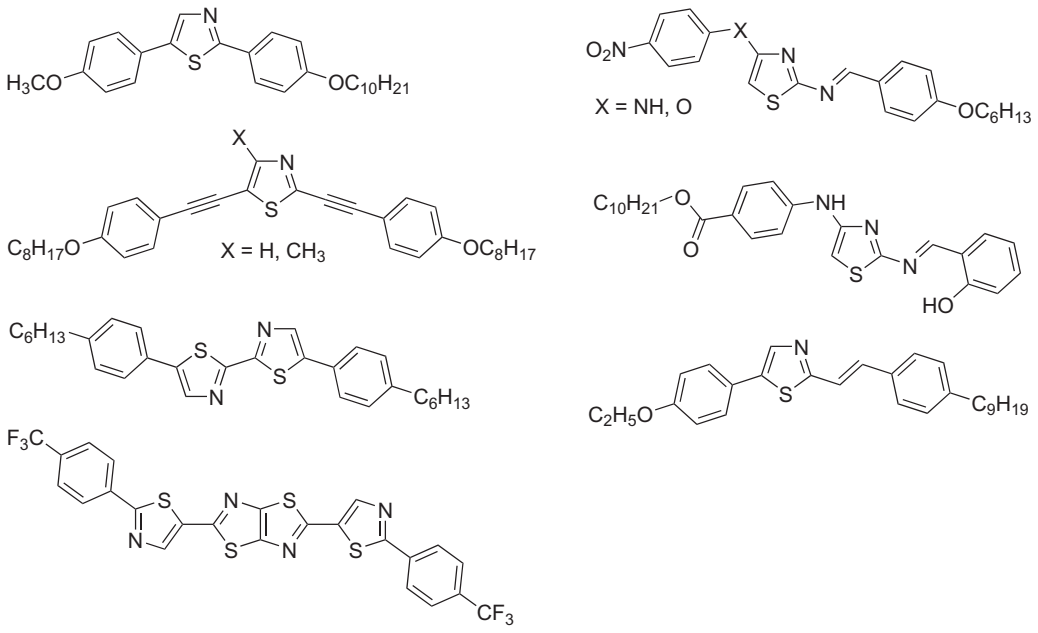


Figure 1. A representative selection of known 1,3-thiazole-containing mesogens.

4-pyridyl units) (*31*); these reports utilised Lawesson's reagent in refluxing xylene and toluene, respectively. Subsequent to Lawesson's work, we published the first solvent-free microwave approach to a 5-dodecyloxy-1,3-thiazole derivative in good yield (83%) (*22*).

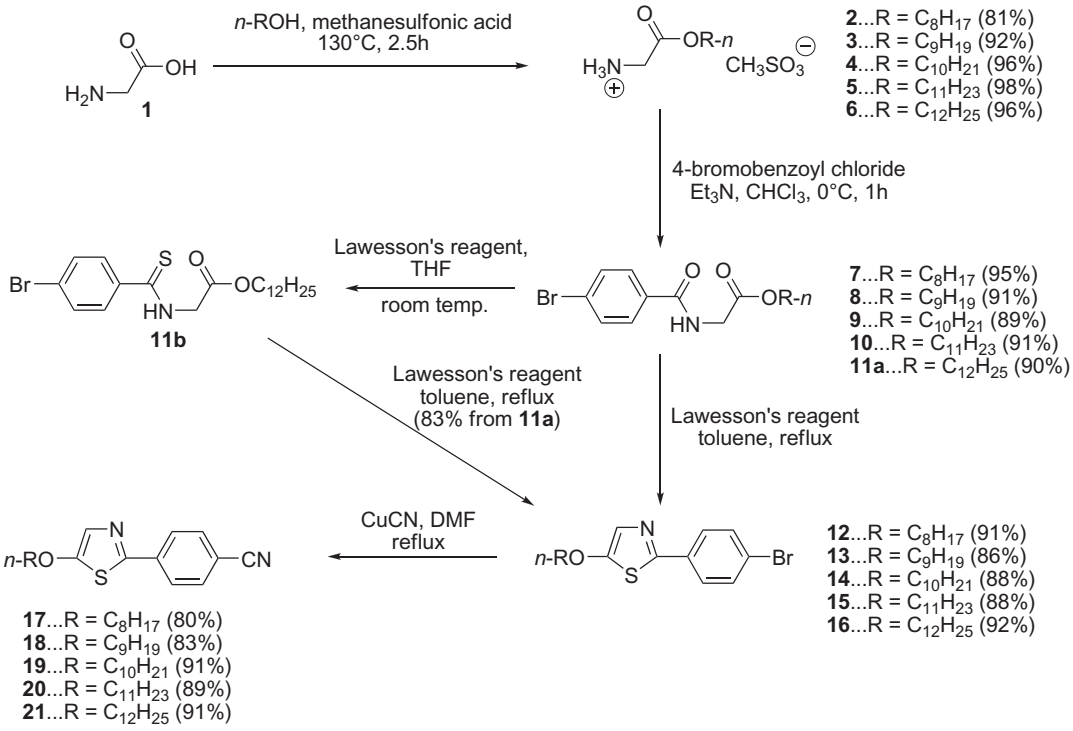
5-Alkoxy-1,3-thiazoles have also been generated via S_NAr chemistry of 5-halo-1,3-thiazoles (Br, Cl or F) with alkoxides; methoxy, ethoxy, benzyloxy, trimethoxybenzyloxy and 1,2-isopropylideneglycerol moieties were investigated with yields ranging from 46% to 100% (*32–43*). While yields of 5-alkoxy-1,3-thiazoles generated through this method vary greatly, the length of the alkoxy chain remains very short.

2. Synthesis

As outlined in Scheme 1, α-acylamino esters **7**–**11a** were obtained by first esterifying glycine with the corresponding alcohol (*44*), followed by *N*-acylation with 4-bromobenzoyl chloride. The workup procedure for compound **3** was slightly modified from that of **2** in an attempt to avoid gross contamination from the starting alcohol in the isolated product; the small amount of alcohol that remained was easily removed through recrystallisation.

Previously published work by our group has shown that 5-alkoxy-1,3-thiazoles can be generated in high yield via reaction of an α-acylamino ester with Lawesson's reagent using microwave irradiation (*22*). However, due to the scale at which the reactions reported in this paper would be performed (about 10 g), we chose the more traditional solvent-based reaction to eliminate any potential scale-up issues. Our first attempt at this transformation was in tetrahydrofuran (THF) at room temperature since, in previously unpublished work, we have had good success in synthesising 2,5-diaryl-1,3-thiazoles utilising Lawesson's reagent under such conditions. However, when compound **11a** was reacted with Lawesson's reagent in THF at room temperature, thioamide **11b** was the sole product instead of the desired compound **16**. Similar conditions have previously been employed for the formation of thioamides (*45, 46*). By contrast, in refluxing toluene, compounds **11a** and **11b** could be converted to the desired 1,3-thiazole **16** in good yield (92% and 83% over two steps, respectively) using Lawesson's reagent. Lawesson's reagent was found to be necessary for the transformation of **11b** to **16** – only starting thioamide was recovered after heating **11b** in both refluxing THF and toluene for 5 hours in the absence of Lawesson's reagent.

While Lawesson's reagent is invaluable for generating sulphur-based heterocycles, a common problem with the use of Lawesson's reagent is the removal of the Lawesson's reagent-based by-products. A recent publication reports that this problem may be alleviated through the use of a fluorous derivative of Lawesson's reagent and subsequent fluorous solid-phase extraction (*47, 48*). However, we have found that simply washing



Scheme 1. Synthetic route to 5-alkoxy-2-(4-cyanophenyl)-1,3-thiazole targets **17-21**.

the crude reaction mixture with aqueous KOH followed by recrystallising from EtOH allows for the 5-alkoxy-1,3-thiazole products to be isolated in pure form with little or no loss of product or formation of side products. This protocol also eliminates the need for column chromatography and thus allows for these 1,3-thiazoles to be generated and purified on a large scale.

The aryl bromides (**12**–**16**) so obtained were efficiently converted to the corresponding final nitrile targets **17**–**21** using a modification of a procedure developed by Friedman and Shechter (*49*) where compounds **12**–**16** were reacted with copper cyanide in refluxing dimethylformamide (DMF).

3. Results and discussion

3.1 Transition temperatures

Transition temperatures of the targeted 5-alkoxy-2-(4-cyanophenyl)-1,3-thiazoles (**17**–**21**) are shown in Table 1. Transition temperatures for the analogous 2-alkoxy-5-(4-cyanophenyl)thiophenes (**22**–**24**) (*50*) are shown in Table 2 and those for the analogous 4′-alkoxybiphenyl-4-ylcarbonitriles (**25**–**29**) (*51*) are shown in Table 3.

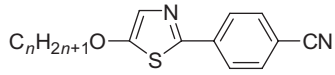
5-Alkoxy-1,3-thiazoles with odd numbers of carbon atoms in the chain (**18** and **20**) were found to be non-mesogenic. It is interesting to note that both the odd and even chain length 5-alkoxy-1,3-thiazoles exhibited very little supercooling (<4°C for odd chain lengths, see experimental details) even at rapid (up to 20°C min^{-1}) cooling rates. As expected, the smectic A mesophase thermal stabilities of these compounds increased with increasing length of the alkoxy chain.

3.1.1 Comparison of alkoxythiazoles with alkoxythiophenes

The 1,3-thiazoles have variable melting points and there does not appear to be any clear relationship between chain length (odd or even) and the melting point of the material. The replacement of thiophene with 1,3-thiazole sometimes results in a reduction of the melting point (compare **19** and **23** [decrease of 3.8°C], **21** and **24** [decrease of 8.6°C]), but this is not a universal trend (compare **17** and **22** [increase of 4.2°C]).

The replacement of thiophene with 1,3-thiazole results in a universal increase in the mesophase thermal stabilities. For the octyloxy compounds (**17** and **22**) both mesogens display monotropic smectic A and nematic phases. Replacement of thiophene with 1,3-thiazole results in a 12.0°C increase in the SmA–N transition and an 8.8°C increase in the N–Iso. Liq. transition. For the decyloxy derivatives

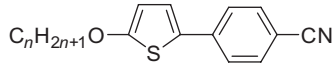
Table 1. Transition temperatures and associated enthalpies *(J/g)* of 5-alkoxy-2-(4-cyanophenyl)-1,3-thiazoles **17–21**.



n	Compound number	Cryst.		SmA		N		Iso. Liq.
8	**17**	•	58.5 *(173.5)*	(•	48.8	•	54.5) *(3.305)*	•
9	**18**	•	67.5 *(197.7)*	–		–		•
10	**19**	•	66.6 *(196.7)*	(•	62.9) *(10.40)*	–		•
11	**20**	•	73.8 *(210.7)*	–		–		•
12	**21**	•	60.5 *(158.9)*	•	68.7 *(21.08)*	–		•

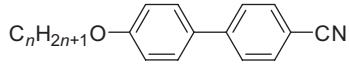
Italicised numbers in parentheses are transition enthalpies (J g^{-1}). No enthalpy is given for the N–SmA transition of **17** as this was not observable by DSC (recrystallisation occurred in tandem with the microscopic observation of SmA phase formation).

Table 2. Transition temperatures 2-alkoxy-5-(4-cyanophenyl)thiophenes **22–24** synthesized by Pantalone.



n	Compound number	Cryst.		SmA		N		Iso. Liq.
8	**22**	•	54.3	(•	36.8	•	45.7)	•
10	**23**	•	70.4	–		(•	36)	•
12	**24**	•	69.1	(•	61.7)	–		•

Table 3. Transition temperatures of 4′-alkoxybiphenyl-4-ylcarbonitriles **25–29** synthesized by Gray.



n	Compound number	Cryst.		SmA		N		Iso. Liq.
8	**25**	•	54.5	•	67.0	•	80.0	•
9	**26**	•	64.0	•	77.5	•	79.5	•
10	**27**	•	59.5	•	84.0	–		•
11	**28**	•	71.5	•	87.5	–		•
12	**29**	•	70.0	•	90.0	–		•

the 1,3-thiazole (**19**) is found to possess a monotropic smectic A phase at 62.9°C while the thiophene derivative (**23**) has a monotropic nematic phase at 36°C. Both dodecyloxy derivatives (**21** and **24**) exhibit smectic A phases although the 1,3-thiazole is enantiotropic and the thiophene is monotropic. In this example, the increase in the smectic A mesophase thermal stability on replacing thiophene with 1,3-thiazole is 7°C. These increases in the mesophase thermal stabilities are consistent with the increased linearity of the 2,5-disubstituted 1,3-thiazole (*1*), which leads to an enhanced aspect ratio.

3.1.2 Comparison of alkoxythiazoles with alkoxyphenyl derivatives

When the phenyl ring is replaced by a 1,3-thiazole ring the melting points are seen to increase for all compounds (compare **17** and **25** [increase of 4.0°C], **18** and **26** [increase of 3.5°C], **19** and **27** [increase of 7.1°C], and **20** and **28** [increase of 2.3°C]) except the dodecyloxy derivative (compare **21** with **29** [decrease of 9.5°C]).

Incorporation of a 1,3-thiazole ring in place of the phenyl ring caused all the observed transition temperatures to decrease. Compounds **17** and **25** (octyloxy derivatives) both have smectic A and nematic phases (monotropic in the case of the 1,3-thiazole and enantiotropic in the case of the phenyl compound). Replacement of the phenyl ring with the 1,3-thiazole results in a decrease of the SmA–N and N–Iso. Liq. transitions by 18.2°C and 25.5°C, respectively. The decyloxy (**19** and **27**) and dodecyloxy (**21** and **29**) derivatives all have smectic A phases and once again are monotropic in the case of the 1,3-thiazole derivatives and enantiotropic in the case of the phenyl derivatives. The clearing points again are seen to decrease upon replacement of the phenyl ring by 1,3-thiazole (compare compounds **19** and **27** [decrease of 21.1°C] and **21** and **29** [decrease of 21.3°C]). Again, these decreases in transition temperatures are consistent with the greater linearity of the biphenyl derivatives.

4. Conclusions

We have demonstrated that long chain 5-alkoxy-1,3-thiazoles can be efficiently generated by reacting α-acylamino esters with Lawesson's reagent. This reaction was found to work well on large scales and the resulting 5-alkoxy-1,3-thiazoles could be obtained in high purity without the use of column chromatography. The developed methodology allowed for the synthesis and analysis of the first series of 5-alkoxy-1,3-thiazole-based liquid crystals. Some of these mesogens showed SmA and N phases, and were found to possess phase transition temperatures that were higher than their thiophene analogues but lower than their phenyl analogues. The observed mesophase thermal stabilities are in accord with the linearity of the system.

5. Experimental

Confirmation of the structures of products was obtained by ^{1}H (400 MHz) and ^{13}C (100 MHz) nuclear magnetic resonance (NMR) (Bruker Avance 400 MHz spectrometer using Topspin version 1.3 software) in $CDCl_3$ with tetramethylsilane as internal standard. Elemental analyses were performed by Atlantic Microlab Inc. (Norcross, GA, USA).

Transition temperatures of the final products were determined by polarising optical microscopy using a Laborlux 12 POLS polarising microscope combined with a Mettler FP82HT Hot Stage and a Mettler FP90 Central Processor. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Differential Scanning Calorimeter 2920 at heating and cooling rates of 5°C min^{-1} (unless otherwise stated) with indium as the internal standard.

Thin layer chromatography was carried out using Whatman brand aluminium-backed plates (250-μm thick layer of 60 Å silica gel with UV 254 nm fluorescence indicator). Column chromatography (flash) was carried out using Silicycle brand 60 Å, 40–63-μm particle size silica.

Et_3N was dried by distilling over CaH_2 and $CHCl_3$ was dried by distilling over P_2O_5. THF was dried by distilling over sodium benzophenone ketyl, and toluene and DMF were dried using 4-Å molecular sieves. Petroleum ether was redistilled. All other chemicals were used as received.

5.1 Octyl 2-aminoethanoate hydromethanesulphonate (2)

Octanol (16.1954 g, 124.360 mmol) and **1** (2.6475 g, 35.267 mmol) were mechanically stirred in an oil bath (external temperature 135°C) for a few minutes before methanesulphonic acid (3.6787 g, 38.276 mmol) was added over about 1 minute and the resulting solution was heated at the same temperature for 2 hours 45 minutes. The cooled solution was then diluted with Et_2O (100 ml) and cooled to −78°C and the resulting white solid was filtered and washed with cold Et_2O (200 ml, −78°C) and dried under vacuum to give an off-white powder (yield = 8.0744 g, 81%), which was sufficiently pure by ^{1}H NMR for the next step. Traces of the starting alcohol were removed by recrystallising from Et_2O. The product was dried *in vacuo* (P_2O_5). Mp = 72.5–73.5°C. ^{1}H NMR: ($CDCl_3$) δ 0.88 (t, J = 6.86 Hz, 3H), 1.20–1.38 (m, 10H), 1.64 (quint., J = 7.02 Hz, 2H), 2.77 (s, 3H), 3.91 (br. q, J = 5.62 Hz, 2H), 4.17 (t, J = 6.84 Hz, 2H), 7.91 (br. s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 25.8, 28.4, 29.19, 29.24, 31.8, 39.0, 40.6, 66.4, 168.0. Anal. Calcd for $C_{11}H_{25}NO_5S$: C, 46.62; H, 8.89; N, 4.94. Found: C, 46.55; H, 8.85; N, 4.92%.

5.2 Nonyl 2-aminoethanoate hydromethanesulphonate (3)

Nonanol (0.8478 g, 5.877 mmol) and **1** (0.1280 g, 1.705 mmol) were stirred in an oil bath (external temperature 130°C) for a few minutes before methanesulphonic acid (0.1921 g, 1.999 mmol) was added dropwise over a few seconds and the resulting solution was heated at the same temperature for 110 minutes. The cooled solution was then diluted with Et_2O (15 ml), cooled in an ice water bath, and allowed to stir at room temperature for 4 hours. During that time, the solution turned clear so it was again cooled in an ice water bath until precipitation occurred at which point it was filtered and washed with Et_2O (15 ml) to give a white solid which was dried *in vacuo* (P_2O_5). Yield 0.4679 g (92%).* Traces of the starting alcohol were removed by recrystallising from Et_2O. Mp = 69.6–70.7°C. ^{1}H NMR: ($CDCl_3$) δ 0.88 (t, J = 6.84 Hz, 3H), 1.20–1.40 (m, 12H), 1.64 (quint., J = 6.97 Hz, 2H), 2.76 (s, 3H), 3.92 (br. q, J = 4.48 Hz, 2H), 4.17 (t, J = 6.85 Hz, 2H), 7.91 (br. s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 28.4, 29.3 (2), 29.5, 31.9, 39.0, 40.6, 66.4, 168.0. Anal. Calcd for $C_{12}H_{27}NO_5S$: C, 48.46; H, 9.15; N, 4.71. Found: C, 48.22; H, 9.01; N, 4.69%. *Using a similar procedure to that described for compound **2** gave a lower yield (8.4719 g, 81%).

5.3 Decyl 2-aminoethanoate hydromethanesulphonate (4)

Compound **4** was prepared using a similar procedure to that described for the preparation of **3** (except that the solution was not cooled prior to being filtered) using the quantities stated: decanol (0.8889 g, 5.616 mmol), **1** (0.1215 g, 1.618 mmol), methanesulphonic acid (0.1972 g, 2.052 mmol). A white solid was obtained which was dried *in vacuo* (P_2O_5). Yield 0.4832 g (96%).* Traces of the starting alcohol were removed by recrystallising from Et_2O and a few drops of EtOH. Mp = 67.4–69.2°C. ^{1}H NMR: ($CDCl_3$) δ 0.88 (t, J = 6.83 Hz, 3H), 1.20–1.38 (m, 14H), 1.64 (quint., J = 6.98 Hz, 2H), 2.76 (s, 3H), 3.91 (br. q, J = 4.79 Hz, 2H), 4.17 (t, J = 6.85 Hz, 2H), 7.94 (br. s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.7, 25.9, 28.6, 29.4 (2), 29.61, 29.64, 32.0, 39.2, 40.8, 66.6, 167.9. Anal. Calcd for $C_{13}H_{29}NO_5S$: C, 50.13; H, 9.39; N, 4.50. Found: C, 49.79; H, 9.23; N, 4.57%. *Using a similar procedure to that described for compound **2** gave a lower yield (9.5980 g, 87%).

5.4 Undecyl 2-aminoethanoate hydromethanesulphonate (5)

Compound **5** was prepared using a similar procedure to that described for the preparation of **3** (except that the solution was not cooled prior to being filtered) using the quantities stated: undecanol (0.9273 g, 5.382 mmol), **1** (0.1167 g, 1.555 mmol), methanesulphonic acid (0.1879 g, 1.955 mmol). A white solid was obtained which was dried *in vacuo* (P_2O_5). Yield 0.4946 g (98%).* Traces of the starting alcohol were removed by recrystallising from Et_2O and a few drops of EtOH. Mp = 77.5–79.1°C. ^{1}H NMR: ($CDCl_3$) δ 0.88 (t, J = 6.84 Hz, 3H), 1.20–1.40 (m, 16H), 1.64 (quint., J = 6.96 Hz, 2H), 2.77 (s, 3H), 3.91 (br. q, J = 5.23 Hz, 2H), 4.17 (t, J = 6.84 Hz, 2H), 7.94 (br. s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 28.4, 29.3, 29.4, 29.55, 29.64 (2), 31.9, 39.1, 40.5, 66.4, 168.0. Anal. Calcd for $C_{14}H_{31}NO_5S$: C, 51.66; H, 9.60; N, 4.30. Found: C, 51.50; H, 9.52; N, 4.30%. *Using a similar procedure to that described for compound **2** gave a lower yield (6.2719 g, 56%).

5.5 Dodecyl 2-aminoethanoate hydromethanesulphonate (6)

Compound **6** was prepared using a similar procedure to that described for the preparation of **2** using the quantities stated: dodecanol (23.1476 g, 124.229 mmol), **1** (2.6506 g, 35.308 mmol), methanesulphonic acid (3.6721 g, 38.207 mmol). An off-white solid was obtained which was dried *in vacuo* (P_2O_5). Yield 11.5367 g (96%). Traces of the starting alcohol were removed by recrystallising from Et_2O and a few drops of EtOH. Mp = 78.1–79.6°C. ^{1}H NMR: ($CDCl_3$) δ 0.88 (t, J = 6.83 Hz, 3H), 1.20–1.40 (m, 18H), 1.64 (quint., J = 7.03 Hz, 2H), 2.77 (s, 3H), 3.91 (br. q, J = 5.48 Hz, 2H), 4.17 (t, J = 6.84 Hz, 2H), 7.96 (br. s, 3H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 28.4, 29.3, 29.4, 29.56, 29.64, 29.66, 29.69, 31.9, 39.1, 40,5, 66.4, 168.0. Anal. Calcd for $C_{15}H_{33}NO_5S$: C, 53.07; H, 9.80; N, 4.13. Found: C, 53.00; H, 9.87; N, 4.13% (in a previous publication (*22*), we inadvertently reported combustion data for the undecyl analogue; the ^{1}H NMR analysis was also missing the signal at δ 4.17).

5.6 Octyl (4-bromobenzoylamino)ethanoate (7)

Compound **7** was prepared using a similar procedure to that described for the preparation of **10** using the quantities stated: **2** (8.00 g, 28.2 mmol), Et_3N (anhydrous, 13.5ml, 97.1 mmol, d = 0.728 g ml^{-1}), $CHCl_3$ (anhydrous, 75 ml), 4-bromobenzoyl chloride (in 30 ml of $CHCl_3$, 6.2644 g, 28.545 mmol). A white solid was obtained which was dried *in vacuo* (P_2O_5). Yield 9.9049 g (95%). Mp 74.3–75.4°C. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.70 Hz, 3H), 1.20–1.40 (m, 10H), 1.67 (quint., J = 6.98 Hz, 2H), 4.19 (t, J = 6.85 Hz, 2H), 4.22 (d, J = 4.95 Hz, 2H), 6.79 (br. t, J = 3.78 Hz, 1H), 7.59

(d, J = 8.49 Hz, 2H), 7.71 (d, J = 8.43 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 25.8, 28.5, 29.2 (2), 31.8, 41.9, 66.0, 126.6, 128.7, 131.9, 132.6, 166.4, 170.1. Anal. Calcd for $C_{17}H_{24}BrNO_3$: C, 55.14; H, 6.53; N, 3.78. Found: C, 55.31; H, 6.55; N, 3.86%.

5.7 Nonyl (4-bromobenzoylamino)ethanoate (8)

Compound **8** was prepared using a similar procedure to that described for the preparation of **10** using the quantities stated: **3** (8.32 g, 28.0 mmol), Et_3N (anhydrous, 13.5 ml, 97.1 mmol, d = 0.728g ml^{-1}), $CHCl_3$ (anhydrous, 75 ml), 4-bromobenzoyl chloride (in 45 ml of $CHCl_3$, 6.2123 g, 28.307 mmol). A white solid was obtained which was dried *in vacuo* (P_2O_5). Yield 9.8273 g (91%). Mp 78.7–79.2°C. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.84 Hz, 3H), 1.20–1.40 (m, 12H), 1.67 (quint., J = 6.99 Hz, 2H), 4.19 (t, J = 7.47 Hz, 2H), 4.22 (d, J = 5.09 Hz, 2H), 6.75 (br. t, J = 3.94 Hz, 1H), 7.57 (d, J = 8.60 Hz, 2H), 7.68 (d, J = 8.55 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 28.5, 29.2 (2), 29.5, 31.9, 41.9, 66.0, 126.6, 128.7, 131.9, 132.5, 166.4, 170.1. Anal. Calcd for $C_{18}H_{26}BrNO_3$: C, 56.26; H, 6.82; N, 3.64. Found: C, 56.42; H, 6.84; N, 3.69%.

5.8 Decyl (4-bromobenzoylamino)ethanoate (9)

Compound **9** was prepared using a similar procedure to that described for the preparation of **10** using the quantities stated: **4** (9.52 g, 30.6 mmol), Et_3N (anhydrous, 14.7 ml, 106 mmol, d = 0.728 g ml^{-1}), $CHCl_3$ (anhydrous, 80 ml), 4-bromobenzoyl chloride (in 32 ml of $CHCl_3$, 6.7630 g, 30.817 mmol). A white solid was obtained which was dried *in vacuo* (P_2O_5). Yield 10.9600 g (89%). Mp 77.1–78.5°C. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.85 Hz, 3H), 1.20–1.40 (m, 14H), 1.67 (quint., J = 6.97 Hz, 2H), 4.19 (t, J = 6.79 Hz, 2H), 4.22 (d, J = 5.02 Hz, 2H), 6.71 (br. t, J = 3.78 Hz 1H), 7.57 (d, J = 8.62 Hz, 2H), 7.71 (d, J = 8.59 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 28.5, 29.2, 29.3, 29.5 (2), 31.9, 41.9, 66.0, 126.6, 128.7, 131.9, 123.6, 166.4, 170.1. Anal. Calcd for $C_{19}H_{28}BrNO_3$: C, 57.29; H, 7.09; N, 3.52. Found: C, 57.15; H, 7.27; N, 3.48%.

5.9 Undecyl (4-bromobenzoylamino)ethanoate (10)

Compound **5** (6.15 g, 18.9 mmol) and Et_3N (anhydrous, 9.5 ml, 68 mmol, d = 0.728 g ml^{-1}) were stirred in $CHCl_3$ (anhydrous, 50 ml) under argon and cooled to 0°C (internal temperature) before a solution of 4-bromobenzoyl chloride (in 20 ml of anhydrous $CHCl_3$, 4.2217 g, 19.237 mmol) was slowly added dropwise over 5 minutes (internal temperature was kept under about 7°C). The resulting solution was stirred at 0°C for 4 hours before being washed with saturated $NaHCO_3$ (120 ml). The aqueous layer was extracted with CH_2Cl_2 (2 × 100 ml) and the organic extracts were combined and washed with brine (75 ml), dried over $MgSO_4$ and concentrated under reduced pressure to give an off-white solid. The resulting off-white solid was dissolved in CH_2Cl_2 (100 ml) and filtered through a 1-inch silica plug with CH_2Cl_2 (400 ml), which gave a white solid that was pure based on ^{1}H NMR. The product was dried *in vacuo* (P_2O_5). Yield 7.0910 g (91%). Mp 81.3–82.0°C. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.85 Hz, 3H), 1.20–1.40 (m, 16H), 1.67 (quint., J = 6.99 Hz, 2H), 4.19 (t, J = 6.79 Hz, 2H), 4.22 (d, J = 5.00 Hz, 2H), 6.70 (br. t, J = 3.88 Hz, 1H), 7.58 (d, J = 8.61 Hz, 2H), 7.68 (d, J = 8.61 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 28.5, 29.2, 29.3, 29.5, 29.57, 29.60, 31.9, 41.9, 66.0, 126.6, 128.7, 131.9, 132.6, 166.4, 170.1. Anal. Calcd for $C_{20}H_{30}BrNO_3$: C, 58.25; H, 7.33; N, 3.40. Found: C, 58.22; H, 7.30; N, 3.37%.

5.10 Dodecyl (4-bromobenzoylamino)ethanoate (11a)

Compound **11a** was prepared using a similar procedure to that described for the preparation of **10** using the quantities stated: **6** (14.87 g, 43.80 mmol), Et_3N (anhydrous, 20.6 ml, 148 mmol, d = 0.728 g ml^{-1}), $CHCl_3$ (anhydrous, 100 ml), 4-bromobenzoyl chloride (in 45 ml of $CHCl_3$, 9.6338 g, 43.898 mmol). A white solid was obtained which was dried *in vacuo* (P_2O_5). Yield 16.8176 g (90%). Mp 83.5–84.6°C. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.82 Hz, 3H), 1.20–1.40 (m, 18H), 1.67 (quint., J = 6.97 Hz, 2H), 4.19 (t, J = 6.80 Hz, 2H), 4.22 (d, J = 4.99 Hz, 2H), 6.69 (br. t, J = 3.86 Hz, 1H), 7.58 (d, J = 8.54 Hz, 2H), 7.68 (d, J = 8.54 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 28.5, 29.2, 29.4, 29.5, 29.6, 29.7 (2), 31.9, 41.9, 66.0, 126.6, 128.7, 131.9, 132.6, 166.4, 170.1. Anal. Calcd for $C_{21}H_{32}BrNO_3$: C, 59.15; H, 7.56; N, 3.28. Found: C, 59.27; H, 7.54; N, 3.28%.

5.11 Dodecyl (4-bromobenzoylthioamido)ethanoate (11b)

Compound **11a** (0.9964 g, 2.337 mmol) was dissolved in THF (anhydrous, 30 ml) while under argon at room temperature. Lawesson's reagent (1.0466 g, 2.5876 mmol) was added to the solution in one portion and the resulting solution was allowed to stir at room temperature for 48 hours. The solution was concentrated under reduced pressure to give a thick, yellow semi-solid, which was dissolved in CH_2Cl_2 (25 ml) and shaken with a solution of KOH (10% wt/vol. 20 ml). The aqueous layer was extracted with CH_2Cl_2 (2 × 20 ml), the organic layers were combined, washed with brine (35 ml), dried over $CaCl_2$ and concentrated

under reduced pressure to give a yellow solid that was found to be relatively pure by ^{1}H NMR (along with a trace of by-products that appear to be related to Lawesson's reagent). Yield 1.2903 g (quant.). ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.84 Hz, 3H), 1.20-1.40 (m, 18H), 1.69 (quint., J = 7.01 Hz, 2H), 4.27 (t, J = 6.70 Hz, 2H), 4.56 (d, J = 4.43 Hz, 2H), 7.57 (d, J = 8.66 Hz, 2H), 7.73 (d, J = 8.66 Hz, 2H), 8.11 (app. br. s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 28.5, 29.2, 29.36, 29.50, 29.56, 29.6 (2), 31.9, 48.1, 66.4, 126.2, 128.3, 131.7, 139.6, 169.1, 197.6.

5.12 2-(4-Bromophenyl)-5-octyloxy-1,3-thiazole (12)

Compound **12** was prepared using a similar procedure to that described for the preparation of **15** using the quantities stated: **7** (8.74 g, 23.6 mmol), Lawesson's reagent (10.5071 g, 25.9774 mmol), toluene (anhydrous, 230 ml). Very light off-white crystals were obtained which were dried *in vacuo* (P_2O_5). Yield 7.91 g (91%). Mp 81.3–82.6°C. ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.83 Hz, 3H), 1.20–1.40 (m, 8H), 1.45 (quint., J = 7.15 Hz, 2H), 1.80 (quint., J = 7.02 Hz, 2H), 4.08 (t, J = 6.52 Hz, 2H), 7.12 (s, 1H), 7.52 (d, J = 8.59 Hz, 2H), 7.66 (d, J = 8.59 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 29.12, 29.19, 29.23, 31.8, 75.5, 123.0, 123.3, 127.0, 132.0, 133.2, 154.0, 162.4. Anal. Calcd for $C_{17}H_{22}BrNOS$: C, 55.43; H, 6.02; N, 3.80. Found: C, 55.34; H, 6.01; N, 3.85%.

5.13 2-(4-Bromophenyl)-5-nonyloxy-1,3-thiazole (13)

Compound **13** was prepared using a similar procedure to that described for the preparation of **15** using the quantities stated: **8** (9.65 g, 25.1 mmol), Lawesson's reagent (11.1775 g, 27.6349 mmol), toluene (anhydrous, 230 ml). An off-white solid was obtained which was dried *in vacuo* (P_2O_5). Yield 8.29 g (86%). Mp 63.0–65.6°C. ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.85 Hz, 3H), 1.20–1.40 (m, 10H), 1.45 (quint., J = 7.14 Hz, 2H), 1.80 (quint., J = 7.02 Hz, 2H), 4.08 (t, J = 6.52 Hz, 2H), 7.12 (s, 1H), 7.52 (d, J = 8.58 Hz, 2H), 7.66 (d, J = 8.59 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 29.1, 29.23, 29.25, 29.5, 31.9, 75.5, 123.0, 123.3, 127.0, 132.0, 133.2, 154.0, 162.4. Anal. Calcd for $C_{18}H_{24}BrNOS$: C, 56.54; H, 6.33; N, 3.66. Found: C, 56.63; H, 6.32; N, 3.62%.

5.14 2-(4-Bromophenyl)-5-decyloxy-1,3-thiazole (14)

Compound **14** was prepared using a similar procedure to that described for the preparation of **15** using the quantities stated: **9** (10.81 g, 27.14 mmol), Lawesson's reagent (12.0784 g, 29.8622 mmol), toluene (anhydrous, 250 ml). Very light, off-white crystals were obtained which were dried *in vacuo* (P_2O_5). Yield 9.48 g (88%). Mp 73.1–75.4°C. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.82 Hz, 3H), 1.20–1.40 (m, 12H), 1.45 (quint., J = 7.15 Hz, 2H), 1.80 (quint., J = 7.02 Hz, 2H), 4.08 (t, J = 6.51 Hz, 2H), 7.12 (s, 1H), 7.52 (d, J = 8.58 Hz, 2H), 7.66 (d, J = 8.59 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 29.1, 29.25, 29.31, 29.5 (2), 31.9, 75.5, 123.0, 123.3, 126.9, 132.0, 133.2, 154.0, 162.4. Anal. Calcd for $C_{19}H_{26}BrNOS$: C, 57.57; H, 6.61; N, 3.53. Found: C, 57.41; H, 6.64; N, 3.56%.

5.15 2-(4-Bromophenyl)-5-undecyloxy-1,3-thiazole (15)

Compound **10** (6.93 g, 16.81 mmol) and Lawesson's reagent (7.4877 g, 18.512 mmol) were dissolved in toluene (anhydrous, 170 ml) while under argon and the resulting solution was heated under reflux for 42 hours (^{1}H NMR showed complete consumption of the starting material – the solution turned a lighter shade of yellow over the course of the reaction) before being concentrated under reduced pressure. Once all the toluene was removed, the light yellow solid was dissolved in CH_2Cl_2 (100 ml) and stirred with KOH (20% wt/vol. 100 ml). A slow resolving emulsion resulted so H_2O (100 ml) was added and after 1 hour the organic layer was drained off and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 ml). The organic layers were combined, washed with brine (100 ml), dried over $CaCl_2$, filtered through celite and concentrated under reduced pressure to give a dark yellow solid. The solid was then recrystallised from EtOH to give white crystals which were dried *in vacuo* (P_2O_5). Yield 6.0843 g (88%). Mp 68.6–69.7°C. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.82 Hz, 3H), 1.20–1.40 (m, 14H), 1.45 (quint., J = 7.14 Hz, 2H), 1.80 (quint., J = 7.02 Hz, 2H), 4.08 (t, J = 6.52 Hz, 2H), 7.12 (s, 1H), 7.52 (d, J = 8.59 Hz, 2H), 7.66 (d, J = 8.59 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 29.1, 29.26, 29.35, 29.52, 29.58, 29.61, 31.9, 75.5, 123.0, 123.3, 127.0, 132.0, 133.2, 154.0, 162.4. Anal. Calcd for $C_{20}H_{28}BrNOS$: C, 58.53; H, 6.88; N, 3.41. Found: C, 58.10; H, 6.86; N, 3.40%.

5.16 2-(4-Bromophenyl)-5-dodecyloxy-1,3-thiazole (16)

Compound **16** was prepared using a similar procedure to that described for the preparation of **15** using the quantities stated: **11a** (9.60 g, 22.5 mmol), Lawesson's reagent (10.0450 g, 24.8349 mmol), toluene (anhydrous, 225 ml). Very light, off-white crystals were obtained which were dried *in vacuo* (P_2O_5). Yield 8.74 g (92%). Mp 76.7–78.1°C. ^{1}H NMR ($CDCl_3$)

δ 0.88 (t, J = 6.84 Hz, 3H), 1.20–1.40 (m, 16H), 1.44 (quint., J = 7.16 Hz, 2H), 1.80 (quint., J = 7.02 Hz, 2H), 4.08 (t, J = 6.52 Hz, 2H), 7.12 (s, 1H), 7.51 (d, J = 8.61 Hz, 2H), 7.66 (d, J = 8.59 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.8, 29.1, 29.3, 29.4, 29.52, 29.57, 29.65 (2), 31.9, 75.5, 122.9, 123.3, 126.9, 132.0, 133.2, 154.0, 162.4. Anal. Calcd for $C_{21}H_{30}BrNOS$: C, 59.43; H, 7.12; N, 3.30. Found: C, 59.52; H, 7.15; N, 3.26%.

5.17 2-(4-Cyanophenyl)-5-octyloxy-1,3-thiazole (17)

Compound **17** was prepared using a similar procedure to that described for the preparation of **20** using the quantities stated: **12** (7.77 g, 21.1 mmol), CuCN (3.6590 g, 40.855 mmol), DMF (anhydrous, 140 ml). A very light yellow solid was obtained which was dried *in vacuo* (P_2O_5). Yield 5.2694 g (80%). Transition temperatures (°C): Cryst. 58.5 (SmA 48.8 N 54.5) Iso. Liq. (Rec. 48.6). ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.86 Hz, 3H), 1.20–1.40 (m, 8H), 1.46 (quint., J = 7.21 Hz, 2H), 1.82 (quint., J = 7.02 Hz, 2H), 4.12 (t, J = 6.51 Hz, 2H), 7.19 (s, 1H), 7.68 (d, J = 8.61 Hz, 2H), 7.89 (d, J = 8.51 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 25.7, 29.09, 29.17, 29.20, 31.8, 75.6, 112.2, 118.6, 123.6, 125.8, 132.7, 138.1, 152.3, 163.8. Anal. Calcd for $C_{18}H_{22}N_2OS$: C, 68.75; H, 7.05; N, 8.91. Found: C, 68.48; H, 7.04; N, 8.83%.

5.18 2-(4-Cyanophenyl)-5-nonyloxy-1,3-thiazole (18)

Compound **18** was prepared using a similar procedure to that described for the preparation of **20** using the quantities stated: **13** (8.12 g, 21.2 mmol), CuCN (3.7242 g, 41.583 mmol), DMF (anhydrous, 140 ml). A very light yellow solid was obtained which was dried *in vacuo* (P_2O_5). Yield 5.8262 g (83%). Transition temperatures (°C): Cryst. 67.5 Iso. Liq. (Rec. 63.9). ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.86 Hz, 3H), 1.20–1.40 (m, 10H), 1.46 (quint., J = 7.14 Hz, 2H), 1.82 (quint., J = 7.02 Hz, 2H), 4.11 (t, J = 6.51 Hz, 2H), 7.19 (s, 1H), 7.68 (d, J = 8.53 Hz, 2H), 7.89 (d, J = 8.53 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.7, 29.1, 29.2 (2), 29.5, 31.9, 75.6, 112.2, 118.6, 123.6, 125.8, 132.7, 138.1, 152.3, 163.8. Anal. Calcd for $C_{19}H_{24}N_2OS$: C, 69.47; H, 7.36; N, 8.53. Found: C, 69.63; H, 7.40; N, 8.47%.

5.19 2-(4-Cyanophenyl)-5-decyloxy-1,3-thiazole (19)

Compound **19** was prepared using a similar procedure to that described for the preparation of **20** using the quantities stated: **14** (9.29 g, 23.4 mmol), CuCN (4.0822 g, 45.581 mmol), DMF (anhydrous, 150 ml). A very light yellow solid was obtained which was dried *in vacuo* (P_2O_5). Yield 7.2822 g (91%). Transition temperatures (°C): Cryst. 66.6 (SmA 62.9) Iso Liq. (Rec. 61.0). ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.83 Hz, 3H), 1.20–1.40 (m, 12H), 1.46 (quint., J = 7.19 Hz, 2H), 1.82 (quint., J = 7.02 Hz, 2H), 4.11 (t, J = 6.52 Hz, 2H), 7.19 (s, 1H), 7.67 (d, J = 8.49 Hz, 2H), 7.89 (d, J = 8.51 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.7, 29.1, 29.2, 29.3, 29.5 (2), 31.9, 75.6, 112.2, 118.6, 123.6, 125.8, 132.7, 138.1, 152.3, 163.8. Anal. Calcd for $C_{20}H_{26}N_2OS$: C, 70.14; H, 7.65; N, 8.18. Found: C, 70.04; H, 7.61; N, 8.06%.

5.20 2-(4-Cyanophenyl)-5-undecyloxy-1,3-thiazole (20)

Compound **15** (5.90 g, 14.4 mmol), CuCN (2.5329 g, 28.282 mmol), and DMF (anhydrous, 100 mL) were stirred and heated under reflux under argon for 24 hours (^{1}H NMR showed complete consumption of starting material) before HCl (3.25M, 100 ml) was slowly added to the cooled solution over about 30 minutes. The resulting mixture was allowed to stir under these conditions for an additional 20 minutes. The purple mixture was then extracted with Et_2O (4 × 100 ml), washed with brine (105 ml), dried over $MgSO_4$ and filtered through a silica plug. The resulting red organic extracts were concentrated under reduced pressure until about 250 ml of the Et_2O remained. Decolourising charcoal (powder, four small scoops) was added to the solution which was then heated under reflux for about 30 minutes. Once cool, the yellow solution was filtered through celite and concentrated under reduced pressure to give a orange solid, which was then recrystallised from EtOH to give a very light yellow solid that was dried *in vacuo* (P_2O_5). Yield 4.5589 g (89%). Approximately 0.5 g of the crude material was subjected to column chromatography (30 g silica, eluent was 20% Et_2O in petroleum ether) to purify further the material for liquid crystal analysis. Transition temperatures (°C): Cryst. 73.8 Iso Liq. (Rec. 70.2). ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.81 Hz, 3H), 1.20–1.40 (m, 14H), 1.46 (quint., J = 7.19 Hz, 2H), 1.82 (quint., J = 7.02 Hz, 2H), 4.11 (t, J = 6.50 Hz, 2H), 7.19 (s, 1H), 7.67 (d, J = 8.46 Hz, 2H), 7.89 (d, J = 8.43 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.7, 29.1, 29.2, 29.3, 29.50, 29.56, 29.60, 31.9, 75.6, 112.2, 118.6, 123.6, 125.8, 132.7, 138.1, 152.3, 163.8. Anal. Calcd for $C_{21}H_{28}N_2OS$: C, 70.75; H, 7.92; N, 7.86. Found: C, 70.85; H, 7.97; N, 7.87%.

15.21 2-(4-Cyanophenyl)-5-dodecyloxy-1,3-thiazole (21)

Compound **21** was prepared using a similar procedure to that described for the preparation of **20** using the quantities stated: **16** (11.79 g, 27.78 mmol), CuCN (4.7256 g, 52.765 mmol), DMF (anhydrous, 180 ml). A very light orange solid was obtained which was dried *in vacuo* (P_2O_5). Yield 9.3367 g (91%). Transition temperatures (°C): Cryst. 60.5 SmA 68.7 Iso Liq. (Rec. 49.5). ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.84 Hz, 3H), 1.20–1.40 (m, 16H), 1.46 (quint., J = 7.17 Hz, 2H), 1.82 (quint., J = 7.02 Hz, 2H), 4.11 (t, J = 6.50 Hz, 2H), 7.19 (s, 1H), 7.67 (d, J = 8.56 Hz, 2H), 7.89 (d, J = 8.57 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 25.7, 29.1, 29.2, 29.4, 29.50, 29.56, 29.64 (2), 31.9, 75.7, 112.2, 118.6, 123.6, 125.8, 132.7, 138.1, 152.3, 163.8. Anal. Calcd for $C_{22}H_{30}N_2OS$: C, 71.31; H, 8.16; N, 7.56. Found: C, 71.50; H, 8.25; N, 7.58%.

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