Synthesis and liquid crystalline property of H-shaped 1,3,4-thiadiazole dimers

Jie Han*, Qiong Wang, Jing Wu and Li-Rong Zhu

Department of Chemistry, Nankai University, Tianjin 300071, China

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Two H-shaped liquid crystalline 1,3,4-thiadiazole dimers D1 and D2 and the corresponding monomers M1 and M2 were synthesised and characterised by 1H/13C nuclear magnetic resonance (NMR) and high-resolution mass spectrometry. The thermal properties of the dimers and monomers were investigated by polarised optical microscopy, differential scanning calorimetry and thermogravimetric analysis. All of these compounds exhibited liquid crystalline behaviours with excellent thermal stabilities. The dimers displayed an enantiotropic or a monotropic nematic phase, while the monomers showed nematic and/or smectic A phases enantiotropically. The nature of the mesophases was determined by the molecular shapes and the terminal groups. Notably, the H-shaped dimers exhibited much lower clearing temperatures than the corresponding rod-like monomers.

Keywords: H-dimer; 1,3,4-thiadiazole; phase transition; synthesis

1. Introduction

Over the past decade, 1,3,4-thiadiazole-based liquid crystals have drawn a continuing interest in display materials and electronic devices due to their excellent thermal stability, electron-deficient nature and photoluminescent properties.[1] Many researchers, for example, Parra,[2,3] Gallardo,[4,5] Sato,[6] Lehmann,[7] Tschierske,[8] Lemieux,[9] Li,[10] Kelly,[11] Tandel,[12] and our research group [13–15] have recently reported various mesogenic 1,3,4-thiadiazole derivatives, and the relationship between the structures and liquid crystalline properties has been investigated intensively. Compared to the bending angle 134° of analogous 1,3,4-oxadiazoles,[16] the 1,3,4-thiadiazole moiety has a larger bending angle of 168°,[17] which makes the molecular shape more linear. In addition, the lateral dipole and polarisability of the sulphur atom are larger than those of the oxygen atom. All of these facts facilitate to form stable thermotropic mesophases with very high melting and clearing points,[17,18] which often bring about some technical difficulty in practical application as well as characterisation of the nature of the mesophases.

Liquid crystalline dimers are referred to the molecules composed of two mesogenic units linked by a flexible spacer. These kinds of materials often exhibited different liquid crystalline behaviour from that of the corresponding monomers and thus attracted intense attention in recent years.[19–22] Among many types of liquid crystalline dimers, the H-shaped ones are special because they can exhibit interesting photoluminescent,[23] electro-optic,[24] photochromism,[25,26] and second-order non-linear properties.[27] In addition, such kinds of liquid crystals usually display lower melting and clearing temperature points owing to the linking spacer.[28,29] In order to develop 1,3,4-thiadiazole-based liquid crystals with low temperature range, two H-shaped dimers D1 and D2 and the respective monomers M1 and M2 were synthesised, and the molecular structures and the reaction conditions are shown in Scheme 1. The thermal behaviours have been investigated with an emphasis on the relationship between the molecular structures and liquid crystalline properties.

2. Results and discussion

The mesomorphic properties of H-shaped dimers D1 and D2 and their corresponding monomers M1 and M2 were studied by polarising optical microscopy (POM) equipped with a hot stage. The mesophases were identified according to the textures observed under POM. All the H-shaped dimers and the monomers displayed enantiotropic or monotropic nematic phases, which were assigned by the typical schlieren textures. For the monomer M2, it further exhibited an enantiotropic smectic A phase with rarely observed oily streak texture.[30] The selected texture pictures are shown in Figure 1. The liquid crystalline properties were also investigated by differential scanning calorimetry (DSC), which are well consistent with the POM observation results. The phase transition temperature and associated enthalpy changes derived from DSC measurements are listed in Table 1 and in the supplementary information (Figure S1–4).

*Corresponding author. Email: hanjie@nankai.edu.cn

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As seen in Table 1, both of the rod-like monomers M1 and M2 exhibited liquid crystalline behaviours in wide temperature ranges with very high clearing points. In sharp contrast, the corresponding H-shaped dimers D1 and D2 have much lower clearing points but narrower mesomorphic temperature ranges. Compared to the rod-like monomers, the distances among the H-shaped molecules become larger and weaken the intermolecular interactions, which may greatly decrease the clearing points as well as the ability to form stable mesophases.[31] The H-shaped dimers can be regarded as monomers with lateral chains, and it is easy to understand the lower clearing enthalpies of the H-dimers.[32] In addition, the H-shaped mesogens exhibit high molecular biaxiality, which may reduce the orientational order at the nematic–isotropic transition and decrease the melting and clearing points greatly.[33,34]

The liquid crystalline behaviours were also affected by the nature of the terminal groups. For example, the monomer M1 exhibited a nematic mesophase, probably because the dynamic nature of the freely rotating methoxy group might coherently destroy the positional orders and result in smaller dipole molecular moment. In the case of M2 with a terminal fluoro substituent, it displayed an additional smectic A mesophase besides the nematic mesophase. The secondary weak interactions such as nonbonded F … F interactions and noncovalent C–H … F hydrogen bonds are believed to stabilise the packing of molecules and lead to the appearance of higher-order smectic A mesophase. The effect of the terminal groups on liquid crystalline properties has also been
The effect of polarisability and shape on thermal behaviours of liquid crystal dimers has also been reported by Yeap et al. recently. The thermogravimetric analysis (TGA) curves of compounds $D_1$, $D_2$, $M_1$ and $M_2$, which show that all these solid samples exhibited no apparent weight loss in the temperature range 25–150°C, indicative of the absence of occluded solvent. All of the solid samples started to lose weight above 320°C in a single step with different onset decomposition temperatures (342°C for $D_1$, 321°C for $D_2$, 343°C for $M_1$, 316°C for $M_2$), which are consistent with the results observed under POM. The thermal stability of this class of compounds is mainly affected by the conjugated core and the terminal groups, while the effect of the molecular shapes on the thermal stability is very slight.

### Table 1. Phase transitions and enthalpies of compounds $D_1$, $D_2$, $M_1$ and $M_2$.

| Compounds | Phase transitions$^{[a]}$ | $T$°C | $\Delta H$ [kJ mol$^{-1}$]$^{[b]}$ |
|-----------|-------------------------|-------|-------------------------------|
| $D_1$ ($R = OCH_3$) | Cr 169.5 (54.8) N 180.8 (1.4) Iso | 120.7 (−52.4) Cr | 179.0 (−2.3) |
| $D_2$ ($R = F$) | Cr$_1$ 129.1 (61.9) Cr$_2$ 136.9 (−35.0) Cr$_3$ 165.7 (46.1) Iso | 101.6 (−36.3) Cr$_2$ 70.3 (−3.4) Cr$_3$ | 161.4 (−0.8) |
| $M_1$ ($R = OCH_3$) | Cr 128.4 (30.0) N 310.8 (1.6) Iso | 91.8 (−30.5) Cr | 307.4 (−1.5) |
| $M_2$ ($R = F$) | Cr$_1$ 125.6 (20.3) Cr$_2$ 137.4 (30.8) SmA 286.8 (1.7) N 295.2 (1.2) Iso | 283.1 (−1.6) SmA 105.2 (−30.5) Cr$_3$ | 292.4 (−1.2) |

Notes: $^{[a]}$SmA = smectic A phase; N = nematic phase; Cr = crystal; Iso = isotropic liquid. $^{[b]}$Derived from the DSC thermogram upon the second heating and the first cooling cycles at the rate of ±10°C min$^{-1}$.

Figure 2 shows thermogravimetric analysis (TGA) curves of compounds $D_1$, $D_2$, $M_1$ and $M_2$, which show that all these solid samples exhibited no apparent weight loss in the temperature range 25–150°C, indicative of the absence of occluded solvent. All of the solid samples started to lose weight above 320°C in a single step with different onset decomposition temperatures (342°C for $D_1$, 321°C for $D_2$, 343°C for $M_1$, 316°C for $M_2$), which are consistent with the results observed under POM. The thermal stability of this class of compounds is mainly affected by the conjugated core and the terminal groups, while the effect of the molecular shapes on the thermal stability is very slight.

## 3. Experimental section

### 3.1 General methods

4-Decyloxybenzoic acid 9 was prepared according to the reported procedure. All other chemicals were commercially available and used as received. Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AVANCE-400 MHz DRX FT-NMR spectrometer (Bruker, Switzerland) with chemical shifts (in ppm) relative to tetramethylsilane. High-resolution electron ionisation mass spectra (HRMS) were recorded by a Finnigan MAT 95 mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA).

The phase transition temperatures and enthalpy changes were measured on a Perkin-Elmer DSC-7a (NETZSCH, Bavaria, Germany) differential scanning calorimeter with a heating rate of 10°C/min and pre-calibrated with a pure indium sample. The optical textures were observed on an optical polarised microscopy OLYMPUS BX51 (OLYMPUS, Tokyo, Japan) equipped with a heating stage. TGAs were performed on a Perkin-Elmer TGA-7 (NETZSCH, Bavaria, Germany) with a heating rate of 10°C/min under a stream of flowing nitrogen.

#### 3.1.1 Synthesis of 2a

To a round-bottom flask were added 4-acyloxybenzoic acid 1a (5.0 g, 27.8 mmol) and thionyl chloride
To a round-bottom flask, the intermediates 2a (5.9 g, 18 mmol) or 2b (5.2 g, 18 mmol), Lawesson’s reagent [2,4-bis-(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulphide] (8.0 g, 19.8 mmol) and dry toluene (40 ml) were added, and the reaction solution was refluxed for 8 h. The solvent were removed under vacuum, and the crude product was recrystallised from dichloromethane to afford 1.4 g of 4a as a yellow solid. Yield, 90%. 1H NMR (400 MHz, CDCl3) δ (ppm) = 7.94 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 3.89 (s, 3H). 13C-NMR (DMSO-d6): δ (ppm) = 167.9, 165.4, 162.2, 153.0, 129.8, 129.3, 127.6, 123.5, 115.4, 56.0, 21.3. HRMS calculated for C15H12N2O2S: 284.0619; found: 284.0687.

3.1.4 Synthesis of 4b
To a round-bottom flask with a solution of 3b (1.6 g, 5.6 mmol) in dry chloroform (20 mL), BBr3 (1.8 g, 7.2 mmol) was added dropwise at −78°C. The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum, and the crude product was recrystallised from dichloromethane to afford 1.4 g of 4b as a yellow solid. Yield, 90%. 1H NMR (400 MHz, CDCl3) δ (ppm) = 7.94 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 3.89 (s, 3H). 13C-NMR (DMSO-d6): δ (ppm) = 167.9, 165.4, 162.2, 153.0, 129.8, 129.3, 127.6, 123.5, 115.4, 56.0, 21.3. HRMS calculated for C15H12N2O2S: 284.0619; found: 284.0687.

3.1.5 Synthesis of 4-decyloxy-2-hydroxybenzoate 6
To a round-bottom flask were added the ester 3a (50 mL), Lawesson’s reagent (2.0 g, 6.0 mmol), KOH (2.2 g), water (4 mL) and ethanol (30 mL), and the reaction solution was refluxed for 6 h. Then, the solution was cooled to room temperature and poured into ice-cooled water (100 mL). The resulting mixture was acidified with diluted HCl to precipitate the crude product, which was collected by filtration, dried and recrystallised from petroleum ether/dichloromethane to yield 1.6 g of 4a as a yellow solid. Yield, 92%. 1H NMR (400 MHz, CDCl3) δ (ppm) = 7.94 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 3.89 (s, 3H). 13C-NMR (DMSO-d6): δ (ppm) = 167.9, 165.4, 162.2, 153.0, 129.8, 129.3, 127.6, 123.5, 115.4, 56.0, 21.3. HRMS calculated for C15H12N2O2S: 284.0619; found: 284.0687.
6.9 g of product as white solid. Yield, 45%. \(^1\)H NMR (400 MHz, C\(\text{DCl}_3\)) \(\delta\) (ppm) = 10.99 (s, 1H), 7.75 (d, \(J = 9.5\) Hz, 1H), 6.49–6.40 (m, 2H), 4.00 (t, \(J = 6.6\) Hz, 2H), 3.94 (s, 3H), 1.87–1.74 (m, 2H), 1.53–1.42 (m, 2H), 1.40–1.25 (m, 12H), 0.91 (t, \(J = 6.7\) Hz, 3H). \(^13\)C NMR (101 MHz, C\(\text{DCl}_3\)) \(\delta\) (ppm) = 170.4, 165.2, 163.8, 131.1, 107.9, 105.2, 101.1, 68.3, 51.9, 31.9, 29.6 (overlap), 29.4, 29.3, 29.0, 26.0, 22.7, 14.1. HRMS calculated for C\(_{18}\)H\(_{28}\)O\(_4\): 308.1988; found: [M + H] 309.2059.

3.1.6 Synthesis of 7

To a round-bottom flask were added 6 (5.0 g, 16.2 mmol), 1,6-dibromohexane (1.85 g, 7.4 mmol), potassium carbonate (10.2 g, 74 mmol), catalytic amount of potassium iodide and N,N-dimethylformamide (70 mL). The reaction mixture was stirred overnight at 80°C. After cooling, it was filtered and the solution was extracted with dichloromethane, washed with brine and dried over MgSO\(_4\). The product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 94/6) to yield 2.1 g 7 as white solid. Yield, 40%. \(^1\)H NMR (400 MHz, C\(\text{DCl}_3\)) \(\delta\) (ppm) = 7.82 (d, \(J = 9.3\) Hz, 2H), 6.46 (m, 4H), 4.02 (t, \(J = 6.4\) Hz, 4H), 3.98 (t, \(J = 6.6\) Hz, 4H), 3.83 (s, 6H), 1.92–1.85 (m, 4H), 1.83–1.73 (m, 4H), 1.63–1.58 (m, 4H), 1.48–1.41 (m, 4H), 1.37–1.25 (m, 24H), 0.88 (t, \(J = 6.7\) Hz, 6H). \(^13\)C NMR (101 MHz, C\(\text{DCl}_3\)) \(\delta\) (ppm) = 166.3, 163.8, 160.8, 133.8, 112.2, 105.1, 100.3, 68.7, 68.2, 51.6, 31.9, 29.6 (overlap), 29.4, 29.3, 29.2, 29.1, 26.0, 25.6, 22.7, 14.1. HRMS calculated for C\(_{42}\)H\(_{66}\)O\(_8\): 698.4758; found: [M + Na]\(^+\) calculated for C\(_{70}\)H\(_{82}\)N\(_4\)NaO\(_{10}\)S\(_2\): 1225.5370; found 1225.5368.

3.1.7 Synthesis of 8

To a round-bottom flask were added a suspension of 7 (2.0 g, 2.9 mmol) in ethanol (30 mL) and a solution of potassium hydroxide (1.6 g, 29 mmol) in water (10 mL), and the reaction mixture was refluxed for 8 h. After cooling to room temperature, the mixture was poured into ice water (50 mL) and neutralised with hydrochloric acid. The crude solids were collected and recrystallised from petroleum ether/ethanol to yield the product 8 (1.8 g, 95%) as white solids. \(^1\)H NMR (400 MHz, C\(\text{DCl}_3\)) \(\delta\) (ppm) = 8.14 (d, \(J = 8.8\) Hz, 2H), 6.66 (d, \(J = 8.9\) Hz, 2H), 6.54 (s, 2H), 4.26 (t, \(J = 6.2\) Hz, 4H), 4.05 (t, \(J = 6.5\) Hz, 4H), 2.04–1.94 (m, 4H), 1.87–1.77 (m, 4H), 1.62–1.59 (m, 4H), 1.53–1.44 (m, 4H), 1.43–1.24 (m, 24H), 0.91 (t, \(J = 6.3\) Hz, 6H).

3.1.8 General procedure for synthesis of D\(_1\), D\(_2\), M\(_1\) and M\(_2\)

These four compounds were prepared according to the same procedure. As an example, the synthesis of D\(_1\) was described as follows. To a round-bottom flask were added the acid 8 (335 mg, 0.5 mmol) and thionyl chloride (10 mL). The mixture was refluxed for 4 h and the excessive SOCl\(_2\) was removed by vacuum distillation, and the residue was dissolved in dry pyridine (10 mL), which was added dropwise to the solution of 4\(_a\) (312 mg, 1.1 mmol) in dry pyridine (10 mL). The reaction mixture was stirred overnight at room temperature. After cooling, the reaction solution was poured into distilled water (50 mL) to precipitate the crude white solid, which was purified by silica gel column chromatography using ethyl acetate/dichloromethane (v/v = 1:10) as an eluent.

D\(_2\): White solid, yield, 67%. \(^1\)H NMR (400 MHz, C\(\text{DCl}_3\)) \(\delta\) (ppm) = 8.03–7.98 (m, 6H), 7.94 (d, \(J = 8.7\) Hz, 4H), 7.31 (d, \(J = 8.7\) Hz, 4H), 7.00 (d, \(J = 8.7\) Hz, 4H), 6.51 (d, \(J = 8.7\) Hz, 2H), 6.47 (s, 2H), 4.05–3.96 (m, 8H), 3.89 (s, 6H), 1.81–1.77 (m, 8H), 1.50–1.39 (m, 4H), 1.39–1.20 (m, 28H), 0.88 (t, \(J = 6.6\) Hz, 6H). \(^13\)C NMR (101 MHz, C\(\text{DCl}_3\)) \(\delta\) (ppm) = 167.9, 166.6, 164.7, 163.6, 161.9, 161.8, 153.3, 134.5, 129.5, 129.0, 127.5, 122.9, 122.8, 114.5, 114.0, 110.6, 105.5, 100.1, 68.7, 68.4, 55.5, 31.9, 29.6, 29.4, 29.3, 29.1, 29.0, 26.0, 25.7, 22.7, 14.1. HRMS (M + Na)\(^+\): calculated for C\(_{70}\)H\(_{82}\)NaO\(_{10}\)S\(_2\): 1225.5370; found 1225.5368.

M\(_1\): White solid, yield, 76%. \(^1\)H NMR (400 MHz, C\(\text{DCl}_3\)) \(\delta\) (ppm) = 8.18 (d, \(J = 8.3\) Hz, 2H), 8.09 (d, \(J = 8.2\) Hz, 2H), 7.99 (d, \(J = 8.3\) Hz, 2H), 7.38 (d, \(J = 8.2\) Hz, 2H), 7.05–7.00 (m, 4H), 4.08 (t, \(J = 6.6\) Hz, 3H), 3.91 (s, 3H), 1.90–1.80 (m, 2H), 1.55–1.19 (m, 14H), 0.91 (t, \(J = 6.6\) Hz, 3H). \(^13\)C NMR (101 MHz, C\(\text{DCl}_3\)) \(\delta\) (ppm) = 168.0, 166.4, 164.6, 163.8, 162.0, 153.1, 132.4, 129.5, 129.1, 127.8, 122.8, 122.7, 121.0, 114.6, 114.4, 68.4, 55.5, 31.9, 29.6, 29.4, 29.3, 29.1, 26.0, 22.0, 14.1. HRMS (M + H)\(^+\): calculated for C\(_{53}\)H\(_{75}\)N\(_4\)NaO\(_{8}\)S: 545.2474; found 545.2478.
M2: Pale yellow solid, yield 54%. 1H NMR (300 MHz, CDCl3) δ (ppm) = 8.16 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.06 (t, J = 6.6 Hz, 3H), 1.89–1.77 (m, 2H), 1.53–1.21 (m, 14H). 13C NMR (101 MHz, CDCl3) δ (ppm) = 167.3, 167.0, 164.4 (d, J = 252.3 Hz), 164.5, 163.8, 153.3, 132.4, 130.0, 129.2, 127.6, 126.5, 122.8, 121.0, 116.4, 68.4, 31.9, 31.0, 29.6, 29.4, 29.3, 29.1, 26.0, 14.1. HRMS (M + H)+: calculated for C31H34FN2O3S: 533.2274; found 533.2260.

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Supplemental data
Supplemental data for this article can be accessed here.

References
[1] Seed A. Synthesis of self-organizing mesogenic materials containing a sulfur-containing five-membered heterocyclic core. J Mater Chem. 2007;35:1779–1777. doi:10.1039/b612666a.
[2] Parra ML, Elgueta EY, Ulloa JA, Vergara JM, Sanchez AI. Columnar liquid crystals based on amino-1,3,4-thiadiazole derivatives. Liq Cryst. 2012;39:917–925. doi:10.1080/02678292.2012.686635.
[3] Elgueta EY, Parra ML, Diaz EW, Barbera J. Synthesis of novel symmetrical tetra- and hexacatenar di-amides containing 1,3,4-thiadiazole units and a study of their mesomorphic and luminescence properties. Liq Cryst. 2014;41:861–871. doi:10.1080/02678292.2014.883446.
[4] Tuzimoto P, Santos DMPO, Moreira TDS, Cristiano R, Bechtold IH, Gallardo H. Luminescent liquid crystals containing a sulphur-based heterocyclic core. Liq Cryst. 2014;41:1097–1108. doi:10.1080/02678292.2014.903003.
[5] Gallardo H, Santos DMPO, Caramori GF, Molin F, Bechtold IH. Synthetic pathway for a new series of liquid crystal 2,6-disubstituted imidazo [2,1-b] [1,3,4] thiadiazole. Liq Cryst. 2013;40:570–580. doi:10.1080/02678292.2013.777977.
[6] Sato M, Matsuoka Y, Yamaguchi I. Bluish-violet light-emitting liquid crystalline hyperbranched polymers using three triisocyanate B3 monomers: preparation, characterization and structure-property relationship. Liq Cryst. 2012;39:1071–1081. doi:10.1080/02678292.2012.696731.
[7] Seltmann J, Marini A, Mennucci B, Dey S, Kumar S, Lehmann M. Nonsymmetric bent-core liquid crystals based on 1,3,4-thiadiazole core unit and their nematic mesomorphism. Chem Mater. 2011;23:2630–2636. doi:10.1021/cm200643u.
[8] Hegmann T, Neumann B, Wolf R, Tschierske C. Liquid crystalline paracyclophanes and ansa compounds – series of polyether macromolecules incorporating diacetylene, phenyl, biphenyl, p-terphenyl and 2,5-diphenyl-1,3,4-thiadiazole rigid cores. J Mater Chem. 2005;15:1025–1034. doi:10.1039/b416091f.
[9] Song Q, Nonnenmacher D, Giesselmann F, Lemieux RP. Tuning 'de Vries-like' properties in siloxane- and carbosilane-terminated smectic liquid crystals. J Mater Chem. 2013;1:343–350. doi:10.1039/c2tc00338d.
[10] Wang H, Bai F-Q, Liu H, Bai B, Ran X, Qu S, Shi J, Xie D, Li H-Y, Li M, Zhang H-X. Experimental and theoretical study on molecular aggregation and its effect on the photo-physical properties of the mesogenic bi-1,3,4-thiadiazole derivative. Phys Chem Chem Phys. 2011;13:9697–9705. doi:10.1039/c1cp20902e.
[11] He CF, Richards GJ, Kelly SM, Contoret AEA, O’Neill M. Heterocyclic polycatenar liquid crystals. Liq Cryst. 2007;34:1249–1267. doi:10.1080/02678290701682373.
[12] Tandel RC, Patel NK. Synthesis and study of liquid crystalline properties of Schiff’s bases having 1,3,4-thiadiazole moiety. Liq Cryst. 2014;41:495–502. doi:10.1080/02678292.2013.859754.
[13] Han J, Chang X-Y, Zhu L-R, Pang M-L, Meng J-B, Chui SS-Y, Lai S-W, Roy VAL. Microwave-assisted synthesis, structure, and tunable liquid-crystal properties of 2,5-diaryl-1,3,4-thiadiazole derivatives through peripheral n-alkoxy chains. Chem Asian J. 2009;4:1099–1107. doi:10.1002/asia.200800440.
[14] Han J, Zhang F-Y, Wang J-Y, Wang Y-M, Pang M-L, Meng J-B. Synthesis and comparative study of the heterocyclic rings on liquid crystalline properties of 2,5-aryl-1,3,4-oxathiadiazole derivatives containing furan and thiophene units. Liq Cryst. 2009;36:825–833. doi:10.1080/02678290903067811.
[15] Han J, Wang J-Y, Zhang F-Y, Zhu L-R, Pang M-L, Meng J-B. Synthesis and nematic behavior of heterocyclic-based liquid crystals containing 1,3,4-oxathiadiazole/thiophene units. J Mater Chem. 2008;35:1205–1214. doi:10.1080/02678290802444129.
[16] Han J. 1,3,4-Oxathiadiazole based liquid crystals. J Mater Chem. 2013;1:7779–7779. doi:10.1039/c3tc31458h.
[17] Han J, Chang X-Y, Zhu L-R, Wang Y-M, Meng J-B, Lai S-W, Chui SS-Y. Synthesis and liquid crystal properties of a new class of calamitic mesogens based on substituted 2,5-diaryl-1,3,4-thiadiazole derivatives with wide mesomorphic temperature ranges. Liq Cryst. 2008;35:1379–1394. doi:10.1080/02678290802617724.
[18] McCairn MC, Kreouzis T, Turner ML. Microwave accelerated synthesis, and evaluation of conjugated oligomers based on 2,5-di-thiophene-[1,3,4]thiadiazole. J Mater Chem. 2010;20:1999–2006. doi:10.1039/b922714h.
[19] Han J, Zhang M, Wang F, Geng Q. Non-symmetric liquid crystal dimers based on 1,3,4-oxathiadiazole derivatives: synthesis, photoluminescence and liquid crystal behavior. Liq Cryst. 2010;37:1471–1478. doi:10.1080/02678292.2010.527382.
[20] Imrie CT, Henderson PA. Liquid crystal dimers and higher oligomers: between monomers and polymers. Chem Soc Rev. 2007;36:2096–2124. doi:10.1039/b714102e.
[21] Imrie CT, Henderson PA, Yeap GY. Liquid crystal oligomers: going beyond dimers. Liq Cryst. 2009;36:755–777. doi:10.1080/02678290903157455.
[22] Seo-C, Han S-T, Win Y-F, Lee S-L, Yeap G-Y. Synthesis and phase transition behavior of new non-symmetric liquid crystal dimers. Liq Cryst. 2014. doi:10.1080/02678292.2014.938373.
[23] Mayoral MJ, Ovejero P, Campo JA, Heras JV, Pinilla E, Torres MR, Lodeiro C, Cano M. Silver and gold luminescent metallomesogens based on pyrazole ligands. Dalton Trans. 2008;6912–6924. doi:10.1039/b808487d.

[24] Medeiros DR, Hale MA, Leitko JK, Willson CG. Laterally linked liquid crystal dimers with electrooptic properties. Chem Mater. 1998;10:1805–1813. doi:10.1021/cm970764m.

[25] Prajapati AK, Varia MC. H-shaped symmetrical twin liquid crystalline compounds with polar-terminal substituents. Liq Cryst. 2013;40:1151–1158. doi:10.1080/02678292.2013.819945.

[26] Varia MC, Kumar S, Prajapati AK. H-shaped azoester-oxymethylene containing twin liquid crystalline compounds. Liq Cryst. 2012;39:365–371. doi:10.1080/02678292.2012.657696.

[27] Zhang Y, Martinez-Perdiguero J, Baumeister U, Walker C, Etxebarria J, Prehn M, Ortega J, Tschierske C, O’Callaghan MJ, Harant A, Handschy M. Laterally azo-bridged H-shaped ferroelectric dimesogens for second-order nonlinear optics: ferroelectricity and second harmonic generation. J Am Chem Soc. 2009;131:18386–18392. doi:10.1021/ja9069166.

[28] Kołpaczyńska M, Madrack K, Mieczkowski J, Górecka E, Pociecha D. H-shaped liquid crystalline dimers. Liq Cryst. 2011;38:149–154. doi:10.1080/02678292.2010.531403.

[29] Kim Y-K, Brecon R, Chakraborty S, Gao M, Sprunt SN, Glesson JT, Twieg RJ, Jäkli A, Lavrentovich OD. Properties of the broad-range nematic phase of a laterally linked H-shaped liquid crystal dimer. Liq Cryst. 2014;41:1345–1355. doi:10.1080/02678292.2014.920930.

[30] Dierking I. Texture of liquid crystals. Weinheim: WILEY-VCH Verlag, GmbH&Co. KGaA; 2003.

[31] Imrie CT, Taylor L. The preparation and properties of low molar mass liquid-crystals possessing lateral alkyl chains. Liq Cryst. 1989;6:1–10. doi:10.1080/0267829890827317.

[32] Chan T-N, Lu Z, Yam W-S, Yeap G-Y, Imrie CT. Non-symmetric liquid crystal dimers containing an iso-flavone moiety. Liq Cryst. 2012;39:393–402. doi:10.1080/02678292.2012.658712.

[33] Lee H-C, Lu Z, Henderson PA, Achard MF, Mahmood WAK, Yeap G-Y, Imrie CT. Cholesteryl-based liquid crystal dimers containing a sulfur-sulfur link in the flexible spacer. Liq Cryst. 2012;39:259–268. doi:10.1080/02678292.2011.641753.

[34] Donaldson T, Staesche H, Lu ZB, Henderson PA, Achard MF, Imrie CT. Symmetric and non-symmetric chiral liquid crystal dimers. Liq Cryst. 2010;37:1097–1110. doi:10.1080/02678292.2010.494412.

[35] Yeap G-Y, Hng T-C, Yeap S-Y, Gorecka E, Ito MM, Ueno K, Okamoto M, Mahmood WAK, Imrie CT. Why do non-symmetric dimers intercalate? The synthesis and characterisation of the α-(4-benzylidene-substituted-aniline-4′-oxy)-ω-(2-methylbutyl-4′-(4″-phenyl)benzoateoxy)alkanes. Liq Cryst. 2009;36:1431–1441. doi:10.1080/02678290903271504.

[36] Han J, Chang X, Wang X, Zhu L, Pang M, Meng J. Microwave-assisted synthesis and liquid crystal properties of 1,3,4-thiadiazole based liquid crystals. Liq Cryst. 2009;36:157–163. doi:10.1080/02678290902752124.