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Synthesis and comparative study of the heterocyclic rings on liquid crystalline properties of 2,5-aryl-1,3,4-oxa(thia)diazole derivatives containing furan and thiophene units

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A series of heterocyclic liquid crystalline compounds containing 1,3,4-oxadiazole/thiadiazole, furan and thiophene units were synthesised and characterised by means of electrospray ionisation-mass spectrometry (ESI-MS), high-resolution mass spectroscopy (HRMS), ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR. The thermal behaviours were investigated by differential scanning calorimetry (DSC) and polarised optical microscopy (POM). The effect of the 1,3,4-oxadiazole, 1,3,4-thiadiazole, furan, thiophene and benzene rings on the liquid crystalline properties was discussed briefly in context with the geometrical and electronic factors. The results showed that the tendency to form mesophases follows the sequence: 1,4-disustituted benzene >2,5-disubstituted thiophene >2,5-disustituted furan and 1,3,4-thiadiazole >1,3,4-oxadiazole.

Keywords: heterocycle; liquid crystals; structure-property relation; synthesis

1. Introduction

The research of liquid crystals (LCs) containing heterocyclic units has attracted much attention in recent years due to greater choices in the design and synthesis of new mesogenic molecules (*1–3*). Among the many kinds of heterocyclic LCs, the 1,3,4-oxadiazole-based mesogens have been studied extensively, because such compounds can not only display LC behaviours with various mesophases (for calamic mesogens see (*4–6*), for disc mesogens see (*7–9*)), but they may also be used as emissive materials and/or electro-transporting/hole-blocking materials in organic light-emitting devices (OLEDs), due to their electron deficiency, high photoluminescence quantum yield, and good thermal and chemical stabilities (*10–12*). Compared to the 1,3,4-oxadiazole unit, the analogous 1,3,4-thiadiazole moiety is also often used to construct rod-like mesogens, which are regarded to be more beneficial in forming stable thermotropic nematic (N) and smectic phases than the 1,3,4-oxadiazole analogues (*13*, *14*). Recently, the effect of the short end groups, the length of the alkoxy/alkyl chains and the mesogenic cores on the mesomorphic properties of 1,3,4-oxadiazole/thiadiazole compounds has been investigated by the authors (*15–17*) and other research groups (*1*, *4*). However, the LCs containing more than one heterocyclic ring, such as 1,3,4-oxadiazole/ thiadiazole, furan and thiophene units in a single molecule, are rarely reported and the effect of the heterocyclic rings on the liquid crystalline properties has not been studied systematically up to now. Herein, we report the synthesis and LC properties of a series of new heterocyclic compounds containing 1,3,4-oxadiazole/thiadiazole, furan or thiophene rings, and the effect of heterocyclic rings on the liquid crystalline properties is discussed.

2. Results and discussion

2.1 Synthesis and characterisation

The synthetic route, as well as the reaction conditions for the target compounds, is shown in Scheme 1. The intermediate 1,3,4-oxadiazole derivatives **POP-Br**, **POF-Br** and **POT′-Br** were obtained in good yields (77–85%) according to the typical procedures reported in the literature (*18*), while the corresponding 1,3,4-thiadiazole analogues **PTP-Br**, **PTF-Br** and **PTT′-Br** were prepared in moderate yields (61–65%), which were carried out by boiling the mixture of the *N,N′*-diacylhydrazines and Lawesson's reagent in anhydrous toluene overnight (*19*). The final products were prepared in high yields (90–94%) by reactions of the corresponding intermediate 1,3,4-oxadiazole derivatives or 1,3,4-thiadiazole analogues with phenylboronic acid according to the typical Suzuki cross-coupling reaction procedure (*20*). All of the target compounds were characterised by means of ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, mass spectrometry (MS) and high-resolution mass spectroscopy (HRMS) techniques. The structure of compound **PTFP** was further confirmed by the single X-ray crystallographic data. It is noted that the aliphatic region of the ^{13}C NMR data of all product compounds shows only nine signals (instead of the expected 10) due to the accidental equivalence, and the aromatic region of the

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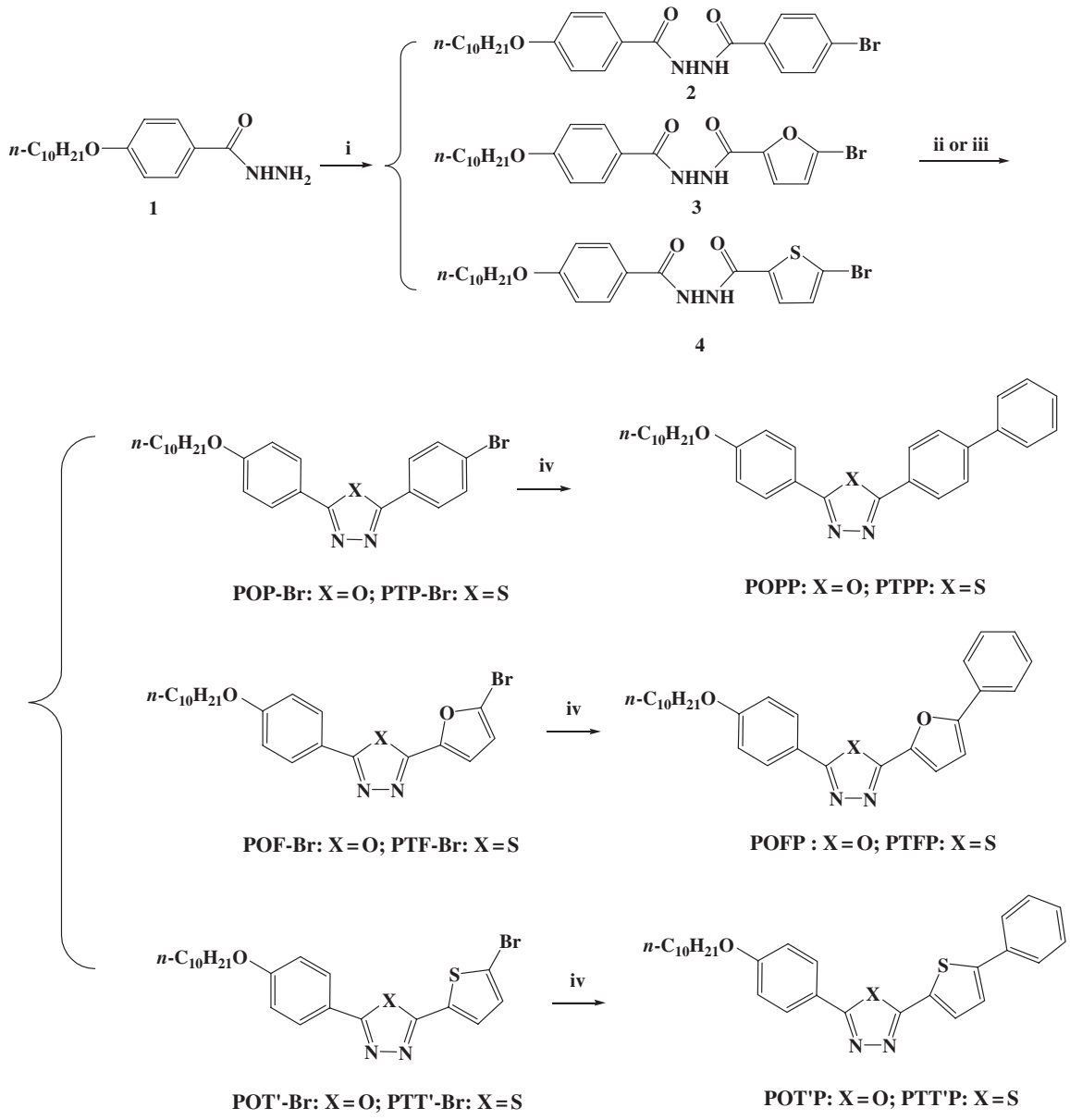

Scheme 1. Reagents and reaction conditions: (i) 4-bromobenzoyl chloride, 5-bromo-2-furoyl chloride, or 5-bromo-2-thiophenecarbonyl chloride, pyridine, overnight, 85–90%; (ii) $SOCl_2$, reflux, 7 h, 77–85%; (iii) Lawesson's reagent, toluene, reflux, 12 h, 61–65%; (iv) phenylboronic acid, K_2CO_3, $PdCl_2(PPh_3)_2$, H_2O, 1,4-dioxane, reflux, 40 min, 90–94%. Note: The symbols **P**, **O**, **T**, **F** and **T′** in the names of the intermediates and final compounds represent benzene, 1,3,4-oxadiazole, 1,3,4-thiadiazole, furan and thiophene rings, respectively.

^{13}C NMR data of compound **POFP** shows only 13 signals (instead of the expected 14), which also may be due to the accidental equivalence.

2.2 Liquid crystalline properties

The liquid crystalline properties were investigated by means of polarised optical microscopy (POM). The mesophases were identified according to the classification system reported by Kumar (*21*) and Dierking (*22*). Among the intermediate compounds, both **POP-Br** and **PTP-Br** exhibited stable liquid crystalline behaviours with different mesomorphic temperature ranges, which have been reported recently by the authors (*17*). As seen in POM observations, neither the 1,3,4-oxadiazole **POF-Br** nor the 1,3,4-thiadiazole **PTF-Br** shows any LC behaviours, while both compounds **POT′-Br** and **PTT′-Br** display an enantiotropic smectic A (SmA) mesophase, which was assigned by the fan-shaped texture as shown in Figure 1(a).

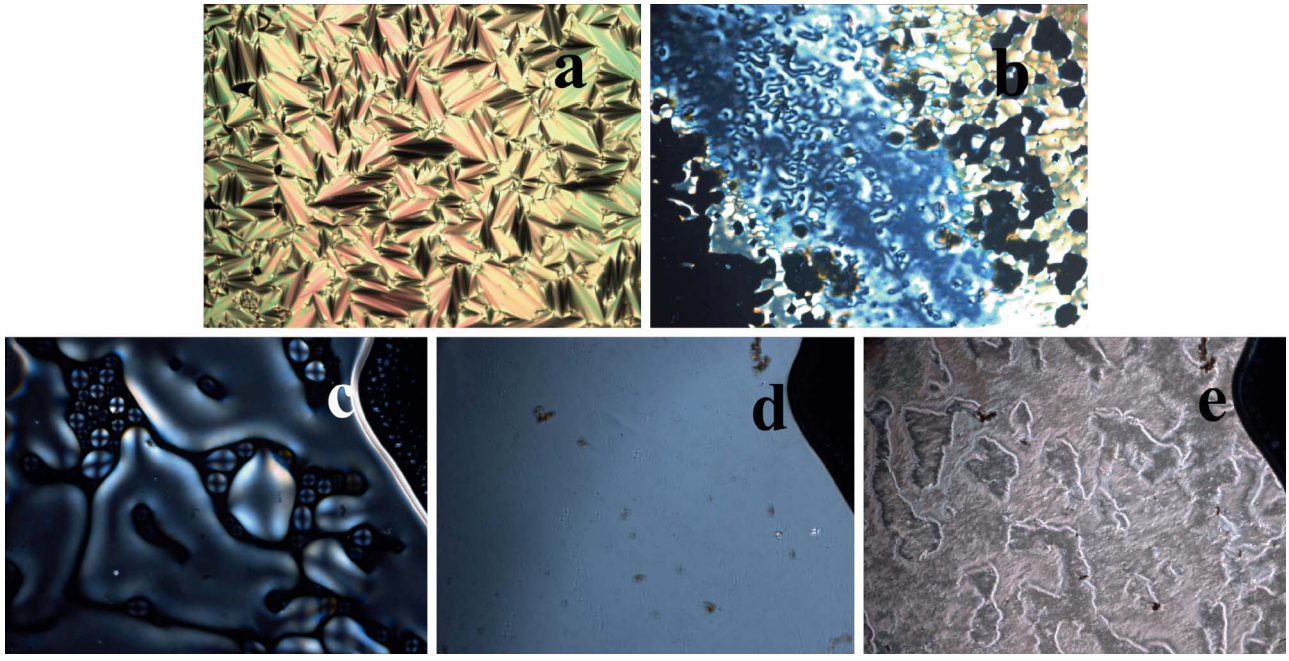

Figure 1. POM images (magnification × 200) in the cooling cycle: (a) SmA mesophase with fan-shaped texture for **PTT′-Br** at 190°C; (b) N mesophase with thread-like texture for **POPP** at 105°C; (c) N mesophase with schlieren texture for **PTPP** at 258.9°C; (d) SmA mesophase with homogeneous texture for **PTPP** at 243.2°C; (e) SmC mesophase for **PTPP** at 156.6°C. Note that (c), (d) and (e) were obtained from the same sample area.

In contrast to the intermediate compounds, the final products have an extended conjugation structure due to the additional phenyl unit; consequently, the liquid crystalline properties of the latter are different from those of the former. As depicted in Table 1, the 1,3,4-oxadiazole-based compound **POPP** only exhibited a monotropic N phase, which was assigned by the typical thread-like texture (Figure 1(b)) observed

Table 1. Phase transition temperatures (T/°C) and enthalpies ΔH/kJ mol^{-1}) of the intermediates and the final products.

Compound	Phase transitions[a] T[°C] (ΔH [kJ mol^{-1}])
POP-Br	Cr_1 61.7 (9.0) Cr_2 117.7 (33.5) SmA 120.6 (7.4) Iso
	Iso 118.7 (–7.1) SmA 102.3 (–16.0) CrE 94.9 (–13.9) Cr_3
PTP-Br	Cr_1 120.9 (38.1) SmA 244.0 (10.0) Iso
	Iso 241.2 (–8.5) SmA 108.4 (–30.3) Cr_2 95.2 (–3.8) Cr_3
POF-Br	Cr_1 86.4 (26.6) Cr_2 94.5 (19.3) Iso 89.4 (–11.8)$Cr_2$73.9 (–13.6) Cr_1
PTF-Br	Cr 106.8 (46.0) Iso 89.3 (–38.4) Cr
POT′-Br	Cr_1 95.3 SmA 101.0 (40.3) Iso[b]
	Iso 98.6 (–5.7) SmA 79.5 (–8.6) Cr_2 44.1 (–10.1) Cr_3
PTT′-Br	Cr 116.9 (29.4) SmA 202.8 (1.0) Iso
	Iso 195.1 (–0.9) SmA 97.9 (–25.1) Cr
POPP	Cr_1 87.3 (1.0) Cr_2 106.9 (6.6) Cr_3 123.6 (30.0) Iso
	Iso 107.2 (–0.8) N 100.0 (–29.9) Cr_4
PTPP	Cr_1 107.1 (14.5) Cr_2 147.4 (25.3) SmC 245.8 (1.1) SmA 261.4 N 263.2 (–1.1)[b] Iso
	Iso 261.0 (–0.7) N 258.5 (–0.3) SmA 240.5 (–0.7) SmC 136.5 (–7.6) Cr_3 133.9 (–9.9) Cr_4
POFP	Cr_1 77.8 (4.0) Cr_2 118.2 (37.0) Iso 102.9 (–36.2) Cr_2 93.4 (–0.7) Cr_1
PTFP	Cr 123.6 (37.2) Iso 106.2 (–38.1) Cr
POT′P	Cr_1 124.1 (22.3) Cr_2 149.4 (32.2) Iso
	Iso 132.5 N 130.5 (–32.2)[b] Cr_3
PTT′P	Cr_1 147.0 (8.3) Cr_2 171.2 (21.2) SmC 203.7 (2.1) SmA 225.5 (1.3) Iso
	Iso 222.9 (–1.3) SmA 198.7 (–1.8) SmC 146.3 (–25.3) Cr_3

[a]Cr_n = crystal phase (nth); SmA = smectic A mesophase; SmC = smectic C mesophase; N = nematic mesophase; Iso = isotropic liquid.
[b]Combined enthalpies.

under POM upon cooling the isotropic liquid. Compared to **POPP**, the 1,3,4-thiadiazole analog **PTPP** exhibited much more complicated liquid crystalline behaviours. Smectic C (SmC), SmA and N mesophases were observed by POM upon heating the solid sample of **PTPP**. The assignments of mesophases were further confirmed by the texture changes in the cooling cycle. Figure 1(c)–(e) shows the phase transitions upon cooling the isotropic liquid of **PTPP** with the same sample area. As depicted in Figure 1(c), birefringent drops and then a schlieren texture were observed at 259.9°C in the cooling cycle, which were typical for the N phase. Further cooling resulted in the formation of a strongly homeotropic SmA (Figure 1(d)) and a schlieren SmC phase (Figure 1(e)) in sequence. Notably, the SmC phase was highly coloured at lower temperatures, but became silvery as the SmC–SmA transition approached; similar phenomena were also reported in the literature (*23*). Both **POFP** and **PTFP** contain a central furan ring and showed no mesophase with the POM observations. The structural characteristic of compounds **POT′P** and **PTT′P** is that they both contain a central thiophene ring, which consequently gives different liquid crystalline properties from the other final products in this work. The 1,3,4-oxadiazole **POT′P** displayed a monotropic N mesophase with very narrow temperature range, while the corresponding 1,3,4-thiadiazole **PTT′P** exhibited enantiotropic SmC and SmA mesophases with wide temperature ranges, which were assigned according to the typical schlieren and fan-shaped textures observed under POM, respectively.

The thermal properties of the intermediate compounds and the final products were investigated by means of differential scanning calorimetry (DSC). The phase transition temperatures and associate enthalpies of these compounds are summarised in Table 1. All of the DSC results are reasonably consistent with the respective POM observations. As representative examples, the DSC thermograms and the phase transitions of **PTPP** and **PTT′P** are depicted in the Figure 2. It is worth noting that all of the DSC thermograms show clear-cut peaks and the baselines are quite flat, both on heating and cooling runs, although the temperature ranges of the thermograms are very wide.

2.3 Discussion

2.3.1 Effect of the heterocyclic 1,3,4-oxadiazole and 1,3,4-thiadiazole rings on liquid crystalline properties

By comparison of the liquid crystalline properties of the 1,3,4-oxadiazoles and the analogous 1,3,4-thiadiazoles in this work, it is apparent that the latter are more favourable for forming calamitic mesophases with a wide mesomorphic temperature range than the former. This might be explained from the geometrical and electronic factors of the molecules. On one hand, according to the single crystal structures of 2,5-diaryl-1,3,4-oxadiazoles/1,3,4-thiadiazoles reported in the literature (*17*, *24–26*), it is well known that the 1,3,4-thiadiazole compounds facilitate to form rod-like structures with large bent angles (ca. 167°–169°) and enable more efficient and closer packing of molecules in the mesophase than the corresponding 1,3,4-oxadiazole analogues with a bent angle of ca. 134°. On the other hand, the electronegativity of sulphur (2.5) is smaller than that of oxygen (3.5), while the sulphur atom is significantly larger than the oxygen atom (the covalent radii are 1.04 Å and 0.66 Å, respectively) (*27*). Consequently, the introduction of a sulphur atom into the molecular structure of the compounds is more helpful in increasing the molecular linearity and polarisability than that of an oxygen atom, which is regarded as playing a very important role in the intra- and inter-molecular interactions that predominantly influence the mesophase stability. In the literature, Parra *et al.* (*1*) also explained the reason why the 1,3,4-thidiazole derivatives are more favourable for forming mesophases than the corresponding 1,3,4-oxadiazole analogues by means of semi-empirical calculations.

2.3.2 Effect of the 1,4-benzene, 2,5-furan and 2,5-thiophene rings on liquid crystalline properties

As stated above, the geometrical structure of the molecule plays a very important role in the intra- and inter-molecular interactions, and thus determines the molecular packing and the mesophase stability. Herein, compounds **PTPP**, **PTFP** and **PTT′P** were chosen as examples to discuss the effect of 1,4-benzene, furan and thiophene rings on the liquid crystalline properties. Among these three compounds, **PTPP** exhibited the richest mesophases with the widest mesomorphic temperature ranges and the highest clearing point. The introduction of the 2,5-furan heterocycle as a replacement for 1,4-benzene in **PTPP** resulted in the disappearance of LC properties in **PTFP**; however, the introduction of the 2,5-thiophene heterocycle as a replacement for the 1,4-benzene unit created stable mesophases in **PTT′P**. The difference in the liquid crystalline properties of these three compounds may be mainly due to the different 1,4-benzene, 2,5-furan and 2,5-thiophene units in their molecular structures. As shown in Figure 3, the bent angles derived from these three structural motifs are 180°, 129.5° and 147.5° (*28*), respectively. Consequently, the molecular linearity of the molecules tends to decrease according to the order of **PTPP** > **PTT′P** > **PTFP**, and the ability to form mesophases of these compounds

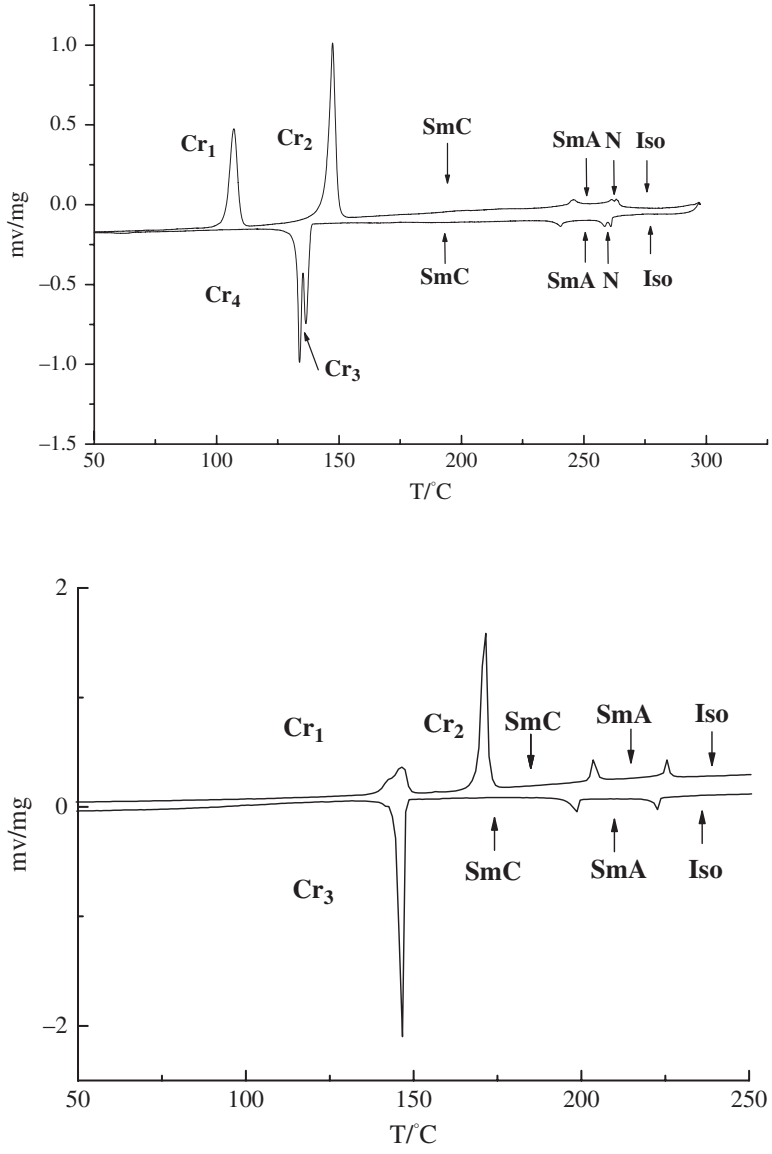

Figure 2. DSC curves of (a) **PTPP** and (b) **PT′TP** at a heating and cooling rate of 5°C min^{-1}.

follows the same sequence. The furan ring is detrimental to mesophase formation due to the very bent nature of the molecular shape, which is consistent with the results reported in the previous literature. (*27*, *29–31*) Of course, the electronic factors, such as anisotropic dispersion interactions and the dipole–dipole attractions, also influence the stability of the mesophase; however, it is impossible to discuss this deeply at present due to lack of relevant data.

In order to study the relationship between the structures and liquid crystalline properties deeply, attempts to obtain single crystals of the final product were carried out and a single crystal, isolated as a yellow platelike of **PTFP** suitable for X-ray diffraction analysis, was slowly grown from CH_2Cl_2 solution. Some selected X-ray crystallographic data are summarised in Table 2 and Figure 4 shows the molecular structure with the atomic numbering scheme of the molecule. When viewed from the side, the four means of the thiadiazole, furan, and two benzene rings were nearly coplanar and the overall molecular shape looks like a 'hockey stick' due to the two attached heterocyclic rings with bend angles of 167° and 129.5°. Therefore, the molecular shape of **PTFP** deviates greatly from the linear structure, which may be the main reason for the non-mesogenic properties of compound **PTFP**.

3. Experimental

3.1 General

Solution ^1H NMR and ^{13}C NMR spectra were recorded on a Varain Mercury Plus 400 (400 M),

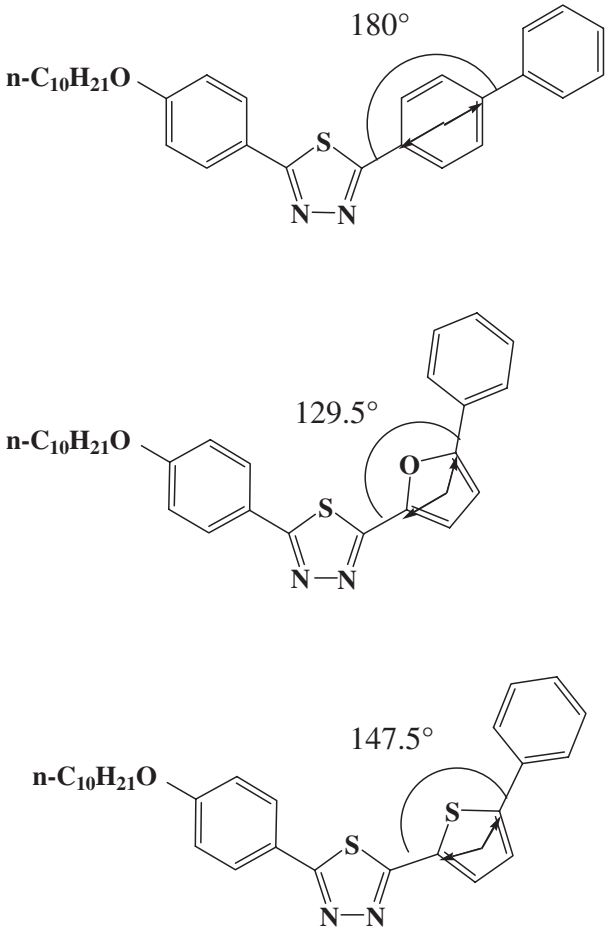

Figure 3. Bond angles of 1,4-benzene, furan and thiophene.

Table 2. Crystallographic data for compounds **PTFP**.

Compound	**PTFP**
Formula	$C_{28}H_{32}N_2O_2S$
Formula weight	460.62
T/K	113(2) K
Space group	Monoclinic, P2(1)/c
a/Å	*a* = 9.2917(19)
b/Å	*b* = 16.569(3)
c/Å	*c* = 16.273(3)
α/°	alpha = 90
β/°	beta = 97.08(3)
γ/°	gamma = 90
V/Å^3	2486.23(9)
Z	4
μ (mm^{-1})	0.157
F (000)	984
Crystal size (mm)	0.14 × 0.12 × 0.10
θ, range for data	1.76–25.01 deg
Reflns collected/unique	13851/4332[*R*(int) = 0.2498
$R[F^2 > 2\sigma(F^2)]$	R_1 = 0.1862
$wR(F^2)$, all data	wR_2 = 0.4778

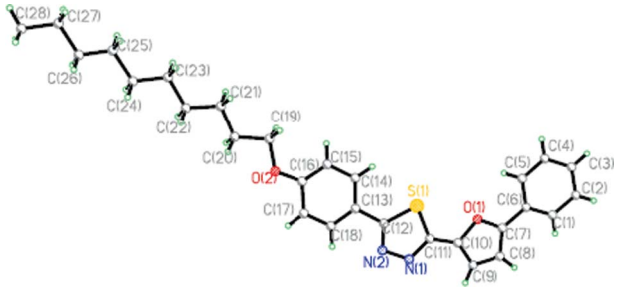

Figure 4. ORTEP drawing of **PTFP** (30% ellipsoids) with atomic numberings.

Bruker AV400 (400 M) or a Bruker AV300 (300 M) spectrometer. Chemical shifts are reported in ppm downfield of tetramethylsilane (TMS). Mass spectra were obtained on a Finnigan LCQ Advantage spectrometer in electrospray ionisation (ESI) mode. The intensity data of crystal of **PTFP** were collected using a Rigaku single crystal X-ray diffractometer with graphite-monochromatised MoK_α radiation (λ = 0.71073 Å) and a Saturn charge-coupled device (CCD) area detector. The X-ray data were collected at 113°C and a maximum 2θ value of 50.02° was obtained. The X-ray crystal structure was solved by the direct method and expanded using the Fourier syntheses technique. All of the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated from idealised geometry of the attached parent atoms and the positions of the thermal parameters were refined using a riding model. Structural refinement based on the full-matrix least-squares refinement on $|F|^2$ values was performed by using the SHELXL97 suite program (*32*). The phase transition temperatures and enthalpy changes were measured on a NETZSCH DSC 204 differential scanning calorimeter at a heating rate of 5°C min^{-1} and calibrated with a pure indium sample. The POM texture image of the mesophase was recorded using a polarised-light optical microscope (OLYMPUS BX51) equipped with a temperature-controlled hot stage.

3.2 *Synthesis*

The starting material *N*-(decyloxybenzoyl)hydrazide **1** and the reaction intermediate compounds **2, POP-Br** and **PTP-Br** were prepared according to the literature procedures (*17*). All other chemicals were commercially available and used as received. The solvents used for the synthesis and column chromatography were of analytical grade. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck, Silica gel F_{254}).

3.2.1 *Preparation of **3** and **4***

The preparation of the intermediates **3** was according to our previously reported method (*17*). 5-bromo-2-furoic acid (1.75 g, 10 mmol) and thionyl chloride $SOCl_2$ (10 ml) were added to a round bottom flask (100 ml) and the mixture was refluxed for 5 h to give the corresponding 5-bromo-2-furoyl chloride. Excessive $SOCl_2$ was removed by vacuum distillation and *p*-decyloxybenzoic hydrazide (10 mmol, 2.92 g) dissolved in pyridine (15 ml) was added dropwise to the as-formed 5-bromo-2-furoyl chloride. The reaction mixture was stirred at room temperature (RT) for 2 h and then at 70°C for a further 1 h. The crude solid was precipitated by pouring the reaction mixture into distilled water (50 ml) and was then washed with distilled water and recrystallised from ethanol to yield product **3**. Compound **4** was prepared according to the same procedure.

5-Bromo-2-furancarboxylic acid *N*′-(4-decyloxbenzoyl)hydrazide **3**: Yield: 88%. Mp.: 138–139°C. ^{1}H NMR (400 MHz, DMSO-d_6): 10.43 (s, 1H), 10.34 (s, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 3.6 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 3.6 Hz, 1H), 4.03 (t, J = 6.6 Hz, 2H), 1.73 (quintet, J = 6.6 Hz, 2H), 1.46–1.19 (m, 14H), 0.86 (t, J = 6.6 Hz, 3H). Electrospray ionisation-mass spectrometry (ESI-MS): m/z: 463.35 $[M-1]^-$.

5-Bromo-2-thiophenecarboxylic acid *N*′-(4-decyloxbenzoyl)hydrazide **4**: Yield: 85%. Mp.: 174–176°C. ^{1}H NMR (400 MHz, DMSO-d_6): 9.92 (s, 1H), 9.21 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 2.4 Hz, 1H), 7.01 (t, J = 2.4 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 3.99 (t, J = 6.6 Hz, 2H), 1.79 (quintet, J = 6.6 Hz, 2H), 1.51–1.42 (m, 2H), 1.39–1.21 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H). ESI-MS: m/z: 479.33 $[M-1]^-$.

3.2.2 *Preparation of **POF-Br***

Intermediate compound **3** (2.3 g, 5 mmol) was dissolved in 25 ml of $SOCl_2$. The reaction mixture was refluxed for 8 h and the excessive thionyl chloride and solvent were removed by vacuum distillation. The crude solid was collected and washed several times with distilled water and was further purified by silica gel column chromatography using ethyl acetate/dichloromethane (v/v = 1:15) as an eluent to yield the product **POF-Br**. The compound **POT′-Br** was prepared according to the same procedure.

2-(5-Bromo-2-furyl)-5-(4-decyloxyphenyl)-1,3,4-oxadiazole **POF-Br**: white solid, yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 3.6 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 6.54 (d, J = 3.6 Hz, 1H), 4.02 (t, J = 6.4 Hz, 2H), 1.71 (quintet, J = 6.8 Hz, 2H), 1.22–1.52 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H). ESI-MS: m/z: 447.44 $[M+1]^+$.

2-(5-Bromo-2-thienyl)-5-(4-decyloxyphenyl)-1,3,4-oxadiazole **POT′-Br**: white solid, yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 4.0Hz, 1H), 7.15 (d, 1H, J = 4.0 Hz), 7.01 (d, J = 8.8 Hz, 2H), 4.03 (t, 2H), 1.82 (quintet, J = 6.8 Hz, 2H), 1.52–1.43 (m, 2H), 1.41–1.22 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H). 463.29 $[M+1]^+$.

3.2.3 *Preparation of **PTF-Br***

Lawesson's reagent (2.3 g, 5.5mmol) was added to a solution of **3** (2.3 g, 5 mmol) in anhydrous toluene. The reaction mixture was refluxed for 10 h (TLC analysis revealed the completion of the reaction), then the crude product was obtained by removing the solvent *in vacuo* and the residue was purified by silica gel column chromatography using ethyl actate/dichloromethane (1:15) as an eluent to yield the product **PTF-Br**. The compound **PTT′-Br** was prepared according to the same procedure.

2-(5-Bromofuryl)-5-(4-decyloxyphenyl)-1,3,4-thiadiazole **PTF-Br**: **w**hite solid, **y**ield: 61%. ^{1}H NMR (300 MHz, $CDCl_3$): 7.90 (d, J = 8.7 Hz, 2H), 7.14 (d, J = 3.6Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 6.51 (d, J = 3.6 Hz, 1H), 4.01 (t, J = 6.6 Hz, 2H), 1.80 (quintet, J = 6.9 Hz, 2H), 1.52–1.18 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 167.4, 161.7, 156.1, 147.7, 129.5, 125.1, 122.2, 115.1, 114.4, 113.3, 68.3, 31.9, 29.6, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1. ESI-MS: m/z: 463.32 $[M+1]^+$.

2-(5-Bromothienyl)-5-(4-decyloxyphenyl)-1,3,4-thiadiazole **PTT′-Br**: white solid, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.89 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 4.0Hz, 1H), 7.09 (d, J = 4.0 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 1.81 (quintet, J = 6.8 Hz, 2H), 1.51–1.42 (m, 2H), 1.40–1.22 (m, 12H), 0.89 (t, J = 6.8 Hz, 3H). ESI-MS: m/z: 479.22 $[M+1]^+$.

3.2.4 *General procedures for synthesis of the final products*

2-(4-Biphenyl)-5-(4-decyloxyphenyl)-1,3,4-oxadiazole (**POPP**): **POP-Br** (228 mg, 0.5 mmol), phenylboronic acid (92 mg, 0.75 mmol), K_2CO_3 (414 mg, 3 mmol) and $PdCl_2(PPh_3)_2$ (1 μmol) were added to a round bottom flask (100 ml) as a catalyst in a solution mixture of dioxane (3 ml) and water (1 ml), boiled for one hour under nitrogen. The reaction mixture was evaporated *in vacuo*, then the solid residue was extracted by CH_2Cl_2 twice (2 × 10 ml), then dried with anhydrous $MgSO_4$, filtered and concentrated at reduced pressure. The crude product was purified by silica gel column chromatography using CH_2Cl_2/ethyl acetate (v/v = 20:1) as an eluent affording the product (**POPP**). White solid, yield: 93%. ^{1}H NMR (300 MHz, $CDCl_3$): 8.19

(d, J = 8.4 Hz, 2H), 8.08 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 7.2, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.03 (d, J = 8.4 Hz, 2H), 4.04 (t, J = 6.6 Hz, 2H), 1.84 (quintet, J = 6.6 Hz, 2H), 1.56–1.22 (m, 14H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 164.6, 164.0, 162.0, 144.2, 139.9, 129.0, 128.7, 128.5, 128.1, 127.6, 127.2, 127.1, 122.9, 115.0, 66.3, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.7, 14.1. ESI-MS: *m*/*z*: 455.32 $[M+1]^+$, HRMS $[M+Na]^+$ Calculated for $C_{30}H_{34}N_2O_2$: 477.2513; found: 477.2519.

Compounds **PTPP, POFP, PTFP, POTP** and **PTT′P** were prepared according to the same procedure as that for **POPP**.

2-(4-Biphenyl)-5-(4-decyloxyphenyl)-1,3,4-thiadiazole **(PTPP)**: white solid, yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$): 8.13 (d, J = 8.1 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8. 4 Hz, 2H), 7.63 (d, J = 7.2 Hz, 2H), 7.47 (t, J = 7.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.80 (quintet, J = 6.6 Hz, 2H), 1.52–1.19 (m, 14H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 167.9, 166.9, 161.6, 143.6, 139.9, 129.5, 128.9, 128.2, 128.0, 127.8, 127.7, 127.1, 122.7, 115.1, 68.5, 32.0, 29.7, 29.5, 29.5, 29.3, 26.1, 22.8, 14.2. ESI-MS: *m*/*z*: 471.30 $[M+1]^+$, HRMS $[M+Na]^+$ Calculated for $C_{30}H_{34}N_2OS$: 493.2284; found: 493.2283.

2-(5-Phenyl-2-furyl)-5-(4-decyloxyphenyl)-1,3,4-oxadiazole **(POFP):** white solid, yield: 91%. ^{1}H NMR (300 MHz, $CDCl_3$): 8.07 (d, J = 8.7 Hz, 2H), 7.84 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.27 (d, J = 3.6 Hz, 1H), 7.02 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 3.6 Hz, 1H), 4.04 (t, J = 6.6 Hz, 2H), 1.83 (quintet, J = 6.6 Hz, 2H), 1.55–1.23 (m, 14H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 163.9, 162.1, 157.1, 157.0, 138.8, 129.4, 128.9, 128.8, 128.7, 124.6, 115.8, 115.0, 107.2, 68.3, 31.9, 29.6, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1. ESI-MS: *m*/*z*: 445.48 $[M+1]^+$. HRMS $[M+Na]^+$ Calculated for $C_{28}H_{32}N_2O_3$: 467.2305; found: 467.2312.

2-(5-Phenyl-2-furyl)-5-(4-decyloxyphenyl)-1,3,4-thiadiazole **(PTFP)**: yellow solid, yield: 93%. ^{1}H NMR (300 MHz, $CDCl_3$): 7.92 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 7.2 Hz, 2H), 7.42 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.26 (d, J = 3.6 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 3.6 Hz, 1H), 4.00 (t, J = 6.6 Hz, 2H), 1.87 (quintet, J = 6.6 Hz, 2H), 1.54–1.20 (m, 14H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 167.9, 167.0, 161.6, 143.6, 140.0, 129.5, 129.0, 128.4, 128.3, 128.0, 127.7, 127.1, 122.7, 115.1, 68.3, 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1. ESI-MS: *m*/*z*: 461.34 $[M-1]^+$. HRMS $[M+Na]^+$ Calculated for $C_{28}H_{32}N_2O_2S$: 483.2077; found: 483.2077.

2-(5-Phenyl-2-thienyl)-5-(4-decyloxyphenyl)-1,3,4-oxadiazole **(POT′P)**: white solid, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (d, J = 9.2Hz, 2H), 7.77 (d, J = 4.0 Hz, 1H), 7.36 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 4.0 Hz, 1H), 7.02 (d, J = 9.2 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 1.82 (quintet, J = 6.4 Hz, 2H), 1.52–1.44 (m, 2H), 1.42–1.22 (m, 12H), 0.89 (t, J = 6.4Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 164.0, 162.0, 160.2, 148.9, 133.2, 130.3, 129.1, 128.7, 126.1, 124.1, 123.9, 116.0, 115.0, 68.3, 31.9, 29.5, 29.3, 29.3, 29.1, 26.0, 22.6, 14.1. ESI-MS: *m*/*z*: 461.50 $[M+1]^+$. HRMS $[M+Na]^+$ Calculated for $C_{28}H_{32}N_2O_2S$: 483.2077; found: 483.2079.

2-(5-Phenyl-2-thienyl)-5-(4-decyloxyphenyl)-1,3,4-thiadiazole **(PTT′P)**: white solid, yield: 91%. ^{1}H NMR (300 MHz, $CDCl_3$): 7.91 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 4.0 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 4.0 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 1.81 (quintet, J = 6.8 Hz, 2H), 1.51–1.42 (m, 2H), 1.41–1.22 (m, 12H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 167.1, 161.6, 160.9, 148.0, 133.4, 131.6, 130.1, 129.4, 129.1, 128.5, 126.0, 123.7, 122.5, 115.1, 68.3, 31.9, 29.5, 29.3, 29.3, 29.1, 26.0, 22.6, 14.1. ESI-MS: *m*/*z*: 477.23 $[M+1]^+$. HRMS $[M+Na]^+$ Calculated for $C_{28}H_{32}N_2OS_2$: 499.1848; found: 499.1849.

4. Conclusion

In this paper, we have reported the synthesis and liquid crystalline behaviours of a new series of heterocyclic compounds containing 1,3,4-oxadiazole, 1,3,4-thiadiazole, furan and thiophene rings. The relationship between the structures and properties shows that the linear molecules fascinate to form stable mesophases with wide mesomorphic temperature ranges, while the bent-shaped molecules result in the disappearance of mesomorphic properties in all of the compounds containing a central furan ring. The tendency to form mesophases follows the sequence: 1,4-disustituted benzene >2,5-disubstituted thiophene >2,5-disustituted furan and 1,3,4-thiadiazole >1,3,4-oxadiazole.

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 696795. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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