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Synthesis and liquid crystalline properties of substituted 2,5-diaryl 1,3,4-oxadiazole derivatives without flexible chains

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A series of new compounds based on aromatically 2,5-disubstituted 1,3,4-oxadiazoles without flexible chains, formulated as *p*-R–C_6H_4–(OC_2N_2)–(*p*-C_6H_4)$_2$–R′ with (i) R=CH_3O, R′=CH_3O, CH_3S, F, H (Ia–Id), (ii) R=CH_3S, R′=CH_3O, CH_3S, F, H (IIa–IId) and (iii) R=F, R′=CH_3O, CH_3S, F, H (IIIa–IIId) (*p*-C_6H_4 and OC_2N_2 represent a *p*-phenylene spacer and a 1,3,4-oxadiazole ring, respectively), were synthesised and characterised by ^{1}H and ^{13}C NMR, MS and HRMS techniques. Mesomorphic properties were investigated using differential scanning calorimetry and polarizing optical microscopy. All of the target compounds (except Id, IId, IIIc and IIId) exhibited an enantiotropic nematic mesophase with high melting temperatures. The liquid crystalline properties of these compounds were influenced greatly by polarity, steric factors and positions of the terminal groups. The effect of the terminal groups on the liquid crystal properties is discussed.

Keywords: 1,3,4-oxadiazole derivative; structure–property relationship; synthesis

1. Introduction

The structure–property relationship is an important aspect of the discipline of liquid crystals, and research in this field is still receiving considerable attention because such relationships are essential for the design and synthesis of desired liquid crystalline materials with specific properties (*1*). A common feature of thermotropic mesogens is that almost all of them comprise a central rigid core connected to one or more fairly long, straight alkyl or alkoxy chains. Generally, the flexible chains may act as a flexible extension to the rigid core and provide a balance between the rigidity and flexibility in a mesogen, which is crucial to the formation of a mesophase. In addition, the flexible chains are also believed to be responsible for the generation of anisotropy in liquid crystals (*2*). However, flexible terminal substitutents are not always necessary to obtain liquid crystals since some compounds without a flexible chain are also able to form a mesophase. So far, few attempts have been made to synthesise liquid crystalline compounds without flexible chains. Typical examples are the *p*-quinquephenyl analogues (*3–5*), wholly aromatic rod-like macrocyclic mesogens (*6*) and mesomorphic disc-like molecules with only peripheral chloro substituents (*7*). Very recently, Binnemans and co-workers studied the liquid crystalline properties of alkali metal salts of aromatic carboxylic acids, which represent another kind of liquid crystals without flexible chains (*8*). Liquid crystal materials without flexible chains often display mesophases with high crystal–nematic transition temperatures and low viscosity, which may meet the diverse demands for liquid crystal displays (LCDs) (*9, 10*). Moreover, the electrostatic interactions and the molecular packing of the liquid crystals without flexible chains are relatively simple, which make it possible to understand fully the reason for the formation of mesophases.

In the past two decades, liquid crystals based on 2,5-diaryl-1,3,4-oxadiazole derivatives have been studied extensively due to their rich mesophases, good thermal and chemical stability and high photoluminescence quantum yields (*11–13*). Up to now, several mesogenic 1,3,4-oxadiazole derivatives with different molecular geometry, e.g. rod-like (*14–17*), disc-like (*18–20*) and star-shaped (*21, 22*), have been reported and their structure–property relationships investigated. To the best of our knowledge, all the reported mesogenic compounds contain at least one flexible alkyl or alkoxy chain. In order to understand the relationship between the structure and property comprehensively, a series of new 2,5-diaryl-1,3,4-oxadiazole derivatives were synthesised. The synthetic route and the reaction conditions are shown in Scheme 1. The molecular feature of these compounds is that they have no flexible chains; all of them have the same conjugated core bearing two different terminal groups. The liquid crystalline properties of the products were investigated by differential scanning calorimetry (DSC) and polarising optical microscopy (POM). The effect of the terminal groups on the nature of mesophases and mesomorphic temperature ranges is discussed.

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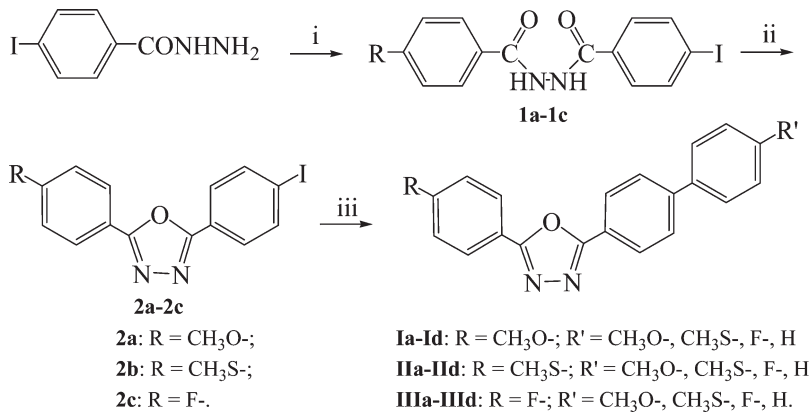

Scheme 1. Synthesis of target compounds. Reagent and conditions: (i) *para*-substituted benzoyl chloride, pyridine, overnight, 88–97%; (ii) $POCl_3$, reflux, 8 h, 75–80%; (iii) *para*-substituted benzylboronic acid, K_2CO_3, $PdCl_2(PPh_3)_2$, H_2O, dioxane, reflux, 40 min, 81–97%.

2. Results and discussion

Synthesis

The 1,3,4-oxadiazole intermediates **2a**–**2c** were prepared using the procedure described in the literature (*15, 23*). *p*-Iodobenzoic hydrazide was coupled with *para*-substituted benzoyl chloride in pyridine to give the resulting amides, which were treated with $POCl_3$ to afford the corresponding 1,3,4-oxadiazole intermediates **2a**–**2c** in 75–80%. In literature, Dingemans *et al.* (*5*) reported the synthesis of oxadiazole and oxazole analogues by using the Suzuki cross-coupling reaction procedures with tetrakis(triphenylphosphine)palladium(0) as catalyst; however, the desired compounds were obtained in only moderate yields due to the rapid decomposition of the palladium catalyst. In this work, the final products were obtained in high yields (81–97%) by also using the Suzuki cross-coupling reaction procedure, but with *trans*-dichlorobis(triphenylphosphine)palladium(II) as catalyst. No decomposition of catalyst was observed in the reactions.

X-ray crystal structure of IIId

Colourless plate-like crystals of **IIId** suitable for X-ray crystallographic analysis were obtained by slow evaporation from a solution in CH_2Cl_2 at room temperature. Figure 1 depicts the X-ray molecular structure of **IIId**. The 1,3,4-oxadiazole ring forms dihedral angles of 1.39 and 9.23° with the two adjacent benzene rings A and B, respectively. The two connected phenylene rings B and C of the biphenylene cores are twisted and form a dihedral angle of 35.1°, so the overall conformation of molecule is not a planar structure. The maximum length and the width of the molecule are 16.097 and 4.067 Å, respectively. Compound **IIId** crystallized a monoclinic space group *P*2(1)/*c* with four molecules per crystallographic asymmetric unit. Non-covalent C–H···F weak hydrogen bonding interactions were observed in the adjacent molecules, whereas the oxygen atoms in the neighbouring 1,3,4-oxadiazole units remain non-interacting, as evidenced by the long O...O contacts (>7.6 Å). Some selected X-ray crystallographic data are summarised in the references and notes (*24*). The XRD data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/tif (CCDC 703848).

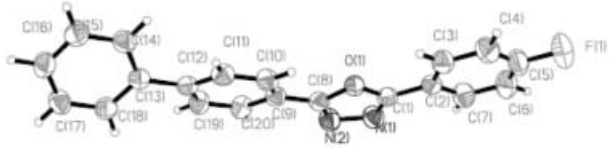

Figure 1. The molecular structure of **IIId** with atomic numbering scheme.

Mesophases and thermal properties

The liquid crystalline behaviour of all final products was investigated by means of POM and DSC. The mesophases were identified according to the classification system reported by Demus and Richter (*25*) and Dierking (*26*). The thermal behaviour of all the target compounds was investigated using DSC. The DSC thermograms were highly consistent with the corresponding observations using POM. The mesophase transition temperatures and associated enthalpy changes of the compounds are summarised in Table 1.

Compounds **Ia**–**Ic**, **IIa**, **IIc** and **IIIb** all displayed an enantiotropic nematic mesophase, which was assigned

Table 1. Thermal properties of all final compounds determined by DSC at a scan rate of 5.0°C min^{-1} (Cr_n=*n*th crystal phase; SmA=smectic A mesophase; N=nematic mesophase; I=isotropic liquid).

Compound	Phase transition	T/°C (ΔH/kJ mol^{-1})
Ia (R=CH_3O, R′=CH_3O)	Cr→N	182.8 (28.2)
	N→I	240.7 (0.4)
	I→N	238.6 (−0.2)
	N→Cr	89.4 (−9.8)
Ib (R=CH_3O, R′=CH_3S)	Cr→N	169.5 (31.0)
	N→I	211.3 (0.3)
	I→N	211.1 (−0.2)
	N→Cr	143.6 (−22.4)
Ic (R=CH_3O, R′=F)	Cr→N	185.6 (36.7)
	N→I	200.4 (0.3)
	I→N	200.0 (−0.3)
	N→Cr	161.3 (−25.3)
Id (R=CH_3O, R′=H)	Cr_1→Cr_2	151.8 (3.3)
	Cr_2→I	156.9 (31.6)
	I→Cr_2	119.4 (−18.4)
	Cr_2→Cr_1	113.1 (−2.1)
IIa (R=CH_3S, R′=CH_3O)	Cr→N	202.9 (42.4)
	N→I	233.1 (0.5)
	I→N	233.0 (−0.4)
	N→Cr	186.9 (−37.0)
IIb (R=CH_3S, R′=CH_3S)	Cr→N	185.6 (39.1)
	N→I	212.5 (0.3)
	I→N	211.5 (−0.4)
	N→SmA	176.4 (−0.6)
	SmA→Cr	169.3 (−34.4)
IIc (R=CH_3S, R′=F)	Cr_1→N	176.0 (26.5)
	N→I	188.5 (0.2)
	I→N	188.0 (−0.3)
	N→Cr_2	167.2 (−12.0)
	Cr_2→Cr_3	162.3 (−6.1)
	Cr_3→Cr_4	158.4 (−2.4)
IId (R=CH_3S, R′=H)	Cr_1→Cr_2	142.9 (9.2)
	Cr_2→I	157.4 (24.5)
	I→Cr	145.4 (−22.9)
IIIa (R=F, R′=CH_3O)	Cr_1→N	196.4 (33.0)
	N→I	234.2 (0.3)
	I→N	233.3 (−0.3)
	N→SmA	161.5 (−0.3)
	SmA→Cr_2	160.7 (−17.9)
	Cr_2→Cr_3	155.3 (−9.6)
IIIb (R=F, R′=CH_3S)	Cr→N	174.4 (27.2)
	N→I	207.8 (0.2)
	I→N	203.1 (−0.2)
	N→Cr	168.8 (−28.8)
IIIc (R=F, R′=F)	Cr→I	195.7 (31.3)
	I→Cr	174.9 (−29.3)
IIId (R=F, R′=H)	Cr→I	172.6 (29.0)
	I→Cr	137.3 (−23.4)

on the basis of textures observed under a polarising optical microscope. As a representative example, Figure 2(a) shows the formation of the nematic phase of **IIIb**. Upon cooling the isotropic liquid, birefringent liquid droplets are formed, and then these droplets coalesce together to give the schlieren texture with two- and fourfold brushes typical of a nematic mesophase. The identity of the nematic mesophase was also

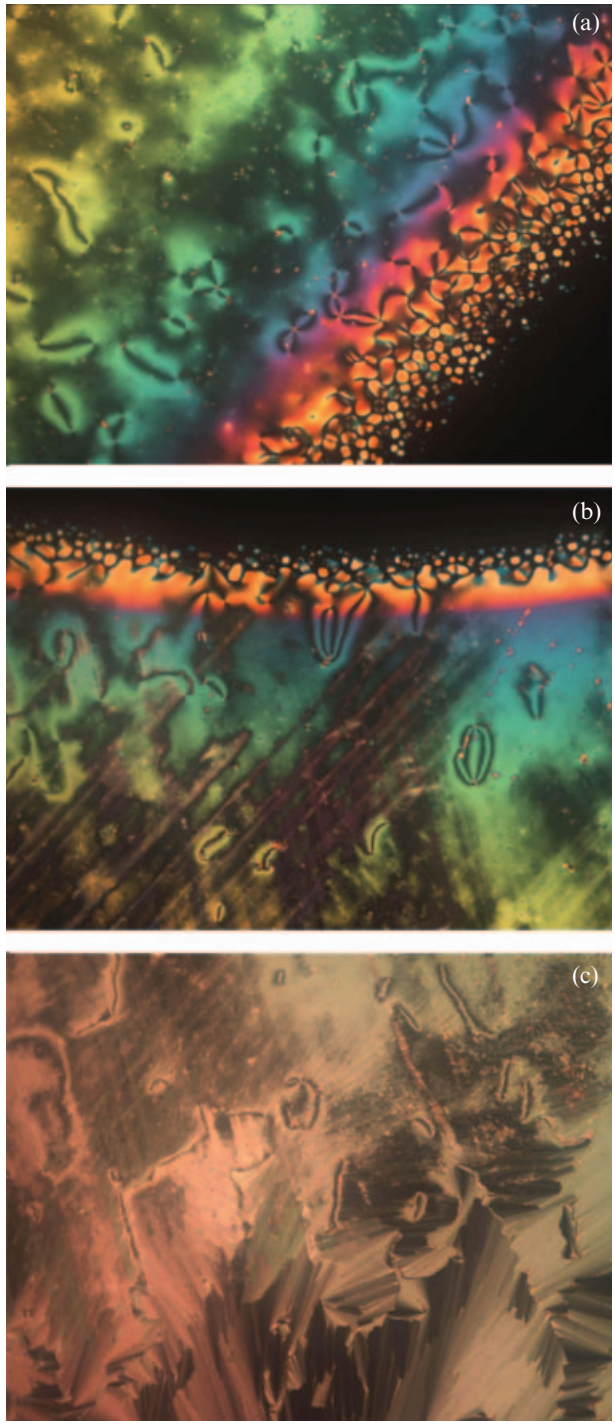

Figure 2. Photomicrographs (200×) of: (a) nematic mesophase with birefringent liquid droplets and twofold and fourfold brush textures for **IIIb** at 205.5°C on heating; (b) nematic mesophase with twofold and fourfold brush textures for **IIIa** at 231.0°C on cooling; (c) transition from schlieren nematic texture to fan-shaped smectic A texture for **IIIa** at 160.5°C on cooling.

confirmed by the transition enthalpy of the clearing point of these compounds. The transition enthalpies of these compounds were in the range 0.2–0.5 kJ mol^{-1},

which are much lower than for a smectic–isotropic transition and typical of a nematic–isotropic transition (*27*). As for compounds **IIb** and **IIIa**, both of them exhibited an enantiotripic nematic phase [Figure 2(b)]; in addition, they also showed a monotropic smectic A (SmA) mesophase with narrow temperature ranges. The SmA mesophase was identified by the transition from schlieren nematic texture to fan-shaped SmA texture, as shown in Figure 2(c). It is worth noting that all of these mesophases exhibit very low viscosities and tend to form homeotropic monodomains.

When one of the two terminal groups was a hydrogen atom or both of the terminal groups are fluorine atoms, the corresponding compounds (**Id**, **IId**, **IIIc** and **IIId**) exhibited no mesomorphic behaviour, only crystal–isotropic transitions were observed.

Effect of the terminal groups on the liquid crystalline properties

Selection of proper terminal groups is a key factor to consider in the design and synthesis of new liquid crystal materials with desired properties. Generally, the terminal groups are believed to play an important role in stabilising the molecular orientations essential for the generation of a mesophase, and the physical properties of liquid crystals are also strongly influenced by the terminal units (*28*). In this work, all the target compounds have the same rigid core bearing two different groups at both ends, so the differences in the liquid crystalline properties of these compounds are solely dependent on the terminal groups. As can be seen in Table 1 and Figure 3, the mesophase stability conferred by the terminal groups is in the order: $-OCH_3 > -SCH_3 > -F > -H$.

The incorporation of dipolar methoxy or methylthio groups on the centrally conjugated core may increase the effective length of the mesogen without altering its breadth significantly, and thus improve the stability of mesophase. As a result, when both of the two terminal groups are methoxy or methylthio groups, the corresponding compounds in this work all exhibit stable liquid crystalline behaviour. It is noted that the methoxy-containing compounds **Ia**, **Ib** and **Id** exhibit lower melting temperature points in comparison with those of the corresponding methylthio-substituted compounds in series II, whereas the methoxy-substituted compounds show higher or comparative clearing temperature points than the corresponding methylthio derivatives. As a result, the methoxy-substituted compounds display stable mesophases with wider temperature ranges than the corresponding methylthio-containing compounds, which may be explained in terms of the larger polarity of methoxy group with respect to the methylthio group. Moreover, the methoxybenzene group adopts a planar structure, whereas the methylthiobenzene group has a non-planar structure with a dihedral angle of 45.3° (*29*). Thus, the methoxy-containing compounds might arrange in ordered packing and facilitate the formation of a stable mesophase. Although fluorine has the largest electronegativity among the four terminal groups, it has a high electron density in its *p* orbitals and thus π back-donation of electrons completes with and partially negates the dipolar attraction of electron density through the σ bond (*30*), which decrease the stability of mesophase and consequently result in no mesomorphic behaviour in compound **IIIc**. It is also easily understood that no mesophases were observed in compounds **Id**, **IId** and **IIId**, because all of these compounds have a non-polar hydrogen atom as one of the terminal groups. It is worth noting that the liquid crystal properties are also influenced by the positions of the terminal groups. For example, compounds **Ic** and **IIIa** are isomers; however, the former exhibited an enantiotropic nematic phase, whereas the latter displayed an enantiotropic nematic phase as well as a monotropic SmA phase. The difference in liquid crystal properties may be tentatively attributed to the different intermolecular interactions and molecular packing caused by the different positions of the terminal groups.

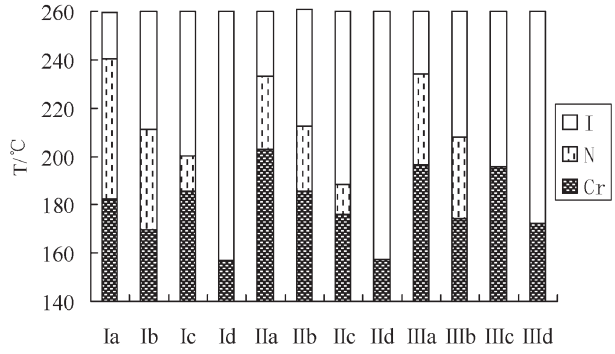

Figure 3. Bar-chart representation of mesomorphic temperature ranges recorded upon heating the solid samples of **Ia**–**Id**, **IIa**–**IId** and **IIIa**–**IIId**.

3. Experimental

General

Solution ^1H and ^{13}C NMR spectra were recorded on Varain Mercury Plus 400 (400 MHz), Bruker AV400 (400 MHz) or Bruker AV300 (300 MHz) spectrometers. Chemical shifts are reported in ppm downfield of tetramethylsilane (TMS). Electrospray-ionisation

(ESI) mass spectra were recorded on a Finnigan LCQ Advantage spectrometer and high-resolution mass spectra (HRMS) were obtained with a Finnigan MAT 95 mass spectrometer. Intensity data for a single crystal of **IIId** with dimensions of $0.60 \times 0.20 \times 0.20$ mm were collected using a Bruker SMART 1000 diffractometer with graphite-monochromatized Mo K_α X-ray radiation ($\lambda = 0.71073$ Å) and Saturn CCD area detector. The X-ray data were collected at a temperature of 293 K and a maximum 2θ value of 50.02° was attained. The X-ray crystal structure was solved by the direct method and expanded using Fourier syntheses technique. All 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 and 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 CrystalStructure or SHELXL97 suite programs (*31*). Thermal properties were measured using DSC (NETZSCH DSC 204) under a nitrogen atomosphere at heating and cooling rates of $5^\circ C\,min^{-1}$ and calibrated with a pure indium sample. Mesophases in the melt were identified using a polarising optical microscope (Olympus BX51) equipped with a temperature control unit and a hot stage, and the samples were placed between two pieces of untreated glass slides using heating and cooling rates of $5^\circ C\,min^{-1}$.

Synthesis

All starting materials were commercially purchased as reagent grade or better and used as received. The solvents used for synthesis were of analytical grade. The Suzuki cross-coupling reactions were performed under a dry atmosphere of nitrogen. Silica gel 60 (Branch of Qingdao Haiyang Chemical Co., Ltd) was used for column chromatography. Thin-layer chromatography (TLC) was performed on silica gel plates (Merck, silica gel F_{254}).

*General procedure for the preparation of the compounds **2a–2c**.*

For 2-(4-iodophenyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (**2a**), *p*-methoxybenzoic acid (5.0 g, 32.9 mmol) was added to 30 ml of phosphorus oxychloride and the mixture was boiling for 6 h. The excess $POCl_3$ was removed by vacuum distillation to give the *p*-methoxybenzoyl chloride. 4-iodobenzhydrazide (8.6 g, 32.9 mmol) was dissolved in 30 ml of dry pyridine and the solution was added to the as-formed *p*-methoxybenzoyl chloride. The resultant reaction mixture was stirred at room temperature overnight and then poured into water to precipitate the intermediate hydrazide derivative (**1a**), which was filtered off, washed thoroughly with distilled water and recrystallised from ethanol twice. Subsequently, the intermediate compounds **1a** was dissolved in 30 ml of $POCl_3$, and the reaction mixture was refluxed for 8 h (TLC analysis revealed the completion of the reaction), then the remaining $POCl_3$ was removed by vacuum distillation. The crude solids were collected and washed several times with distilled water and purified by recrystallisation from ethanol to give the product **2a** as a white solid. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (d, $J = 8.8$ Hz, 2H), 7.94–7.79 (m, $J = 8.8$ Hz, 4H), 7.04 (d, $J = 8.8$ Hz, 2H), 3.90 (s, 3H). MS (EI, m/e, relative intensity, %): 378 (M^+, 100).

Compounds **2b** and **2c** were prepared according to the same procedure as that for **2a**. 2-(4-Iodophenyl)-5-(4-methylthiophenyl)-1,3,4-oxadiazole (**2b**) was obtained as a white solid. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (d, $J = 8.4$ Hz, 2H), 7.91–7.82 (m, $J = 8.8$ Hz, 4H), 7.35 (d, $J = 8.8$ Hz, 2H), 2.55 (s, 3H). ESI-MS: m/z: 395.20 $[M+H]^+$.

2-(4-Iodophenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole (**2c**) was obtained as a white solid. Yield: 78%. ^{1}H NMR (DMSO-d_6, 300 MHz): 8.22–8.18 (m, 2H), 8.03–7.89 (m, 4H), 7.51–7.45 (m, 2H). MS (EI, m/e, relative intensity, %): 366 (M^+, 100).

*General procedures for preparation of the final products **Ia–Id**, **IIa–IId** and **IIIa-IIId**.*

For 2-(4′-methoxy-4-biphenyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (**Ia**), compound **2a** (200 mg, 0.5 mmol), 4-methoxyphenylboronic acid (120 mg, 0.8 mmol), $PdCl_2(PPh_3)_2$ (3.0 μmol), 2M K_2CO_3 (1.5 ml) were added to dioxane (10 m). The mixture boiled for 40 min under a nitrogen atmosphere with magnetic stirring. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (3×10 ml). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography with ethyl acetate/dichloromethane (1:20) as eluent affording **Ia** as a white solid. Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.17 (d, $J = 8.4$ Hz, 2H), 8.10 (d, $J = 8.8$ Hz, 2H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 8.8$ Hz, 2H), 7.08–6.99 (m, $J = 8.8$, 4H), 3.91 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 164.46, 164.13, 162.35, 159.88, 143.86, 132.31, 128.69, 128.22, 127.26, 127.08, 122.22, 116.57, 114.53, 114.46, 55.46, 55.38. ESI-MS: m/z 359.30 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{22}H_{18}N_2O_3$, 381.1210; found, 381.1207.

Compounds **Ib**–**Id**, **IIa**–**IId** and **IIIa**–**IIId** were prepared according to the same procedure as that for **Ia**.

2-(4′-Methylthio-4-biphenyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (**Ib**) was obtained as a white solid. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.19 (d, J=8.4 Hz, 2H), 8.10 (d, J=8.8 Hz, 2H), 7.74 (d, J=8.4 Hz, 2H), 7.59 (d, J=8.4 Hz, 2H), 7.36 (d, J=8.4Hz, 2H), 7.05 (d, J=8.8 Hz, 2H), 3.91 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 164.54, 164.03, 162.36, 143.55, 138.99, 136.45, 128.72, 127.42, 127.32, 127.26, 126.82, 122.72, 116.48, 114.53, 55.48, 15.68. ESI-MS: m/z 375.25 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{22}H_{18}N_2O_2S$, 397.0981; found, 397.0976.

2-(4′-Fluoro-4-biphenyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (**Ic**) was obtained as a white solid. Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.19 (d, J=7.6 Hz, 2H), 8.11 (d, J=8.4 Hz, 2H), 7.71 (d, J=8.0 Hz, 2H), 7.67–7.58 (m, 2H), 7.18 (t, J=8.4 Hz, 2H), 7.05 (d, J=8.4 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 164.56, 164.16, 163.93, 162.38, 161.70, 143.20, 135.99, 135.96, 128.83, 128.75, 128.71, 127.49, 127.31, 122.87, 116.42, 116.02, 115.81, 114.52, 55.47. ESI-MS: m/z 347.27 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{21}H_{15}FN_2O_2$, 369.1010; found, 369.1009.

2-(4-Biphenyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (**Id**) was obtained as a white solid. Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.20 (d, J=8.8 Hz, 2H), 8.10 (d, J=8.8 Hz, 2H), 7.76 (d, J=8.8 Hz, 2H), 7.67 (d, J=7.2 Hz, 2H), 7.50 (t, J=7.6 Hz, 2H), 7.42 (t, J=7.6 Hz, 1H), 7.05 (d, J=9.2 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 164.55, 164.05, 162.40,144.290 139.880, 128.97, 128,72, 128.13, 127.66, 127,28, 127.14, 122.88, 116.52, 114.55, 55.46. ESI-MS: m/z 329.27 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{21}H_{16}N_2O$, 351.1104; found, 351.1111.

2-(4′-Methoxy-4-biphenyl)-5-(4-methylthiophenyl)-1,3,4-oxadiazole (**IIa**) was obtained as a white solid. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.17 (d, J=8.4 Hz, 2H), 8.06 (d, J=8.8 Hz, 2H), 7.72 (d, J=8.4 Hz, 2H), 7.61 (d, J=8.8 Hz, 2H), 7.37 (d, J=8.8Hz, 2H), 7.02 (d, J=8.8 Hz, 2H), 3.88 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 164.36, 159.88, 144.02, 143.94, 132.26, 128.25, 127.36, 127.14, 125.87, 122.051, 120.16, 114.45, 55.41, 15.01. ESI-MS: m/z 375.27 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{22}H_{18}N_2O_2S$, 397.0981; found, 397.0981.

2-(4′-Methylthio-4-biphenyl)-5-(4-methylthiophenyl)-1,3,4-oxadiazole (**IIb**) was obtained as a white solid. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.19 (d, J=8.4 Hz, 2H), 8.06 (d, J=8.8 Hz, 2H), 7.74 (d, J=8.4 Hz, 2H), 7.59 (d, J=8.4 Hz, 2H), 7.38(d, J=2.8 Hz, 2H), 7.35 (d, J=2.4 Hz, 2H), 2.56 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 164.40, 164.23, 144.00, 143.67, 139.06, 136.36, 127.41, 127.38, 127.26, 127.14, 126.80, 125.84, 122.56, 120.08, 15.66, 14.98. ESI-MS: m/z 359.30 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{22}H_{18}N_2OS_2$, 413.0753; found, 413.0758.

2-(4′-Fluoro-4-biphenyl)-5-(4-methylthiophenyl)-1,3,4-oxadiazole (**IIc**) was obtained as a white solid. Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.20 (d, J=8.4 Hz, 2H), 8.06 (d, J=8.4 Hz, 2H), 7.71 (d, J=8.4 Hz, 2H), 7.67–7.58 (m, 2H), 7.37 (d, J=8.4 Hz, 2H), 7.18 (d, J=8.4 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 164.44, 164.14, 164.14, 161.72, 144.05, 143.33, 135.94, 135.91, 128.84, 128.76, 127.51 127.38, 127.13, 125.82, 122.72, 120.03, 116.04, 115.83, 14.96. ESI-MS: m/z 363.29 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{21}H_{15}FN_2OS$, 385.0781; found, 385.0783.

2-(4-Biphenyl)-5-(4-methylthiophenyl)-1,3,4-oxadiazole (**IId**) was obtained as a white solid. Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.21 (d, J=8.4 Hz, 2H), 8.06 (d, J=8.8 Hz, 2H), 7.77 (d, J=8.4 Hz, 2H), 7.66 (d, J=7.2 Hz, 2H), 7.50 (t, J=7.6 Hz, 2H), 7.42 (t, J=7.6 Hz, 1H), 7.37 (d, J=8.4, 2H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 164.41, 164.25, 144.40, 144.38, 144.00, 139.80, 128.99, 128.18, 127.68 127.34, 127.14, 125.84, 122.70, 120.08, 14.98. ESI-MS: m/z 345.25 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{21}H_{16}N_2OS$, 367.0876; found, 367.0875.

2-(4′-Methoxy-4-biphenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole (**IIIa**) was obtained as a white solid. Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.20–8.14 (m, 4H), 7.72 (d, J=8.4 Hz, 2H), 7.61 (d, J=8.8 Hz, 2H), 7.23 (d, J=8.4Hz, 2H), 7.02 (t, J=8.8 Hz, 2H), 7.05 (d, J=8.4 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.04, 164.62, 163.70, 163.52, 159.90, 144.14, 132.16, 129.24, 129.15, 128.24, 127.36, 127.13, 121.85, 120.34, 120.31, 116.54, 116.32, 114.45, 55.39. ESI-MS: m/z 347.25 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{21}H_{15}FN_2O_2$, 369.1010; found, 369.1012.

2-(4′-Methylthio-4-biphenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole (**IIIb**) was obtained as a white solid. Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.23–8.14 (m, 4H), 7.73 (d, J=8.4 Hz, 2H), 7.58 (d, J=8.4 Hz, 2H), 7.35 (d, J=8.4Hz, 2H), 7.23 (d, J=8.8 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.05, 164.48, 163.74, 163.54, 143.78, 139.15, 136.20, 130.63, 129.24, 129.16, 127.38, 127.25, 126.74, 122.31, 120.24, 120.21, 116.54, 116.32, 15.60. ESI-MS: m/z 363.64 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{21}H_{15}FN_2OS$, 385.0781; found, 385.0781.

2-(4′-Fluoro-4-biphenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole (**IIIc**) was obtained as a white solid. Yield:

83%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.23–8.14 (m, 4H), 7.72 (d, J=8.4 Hz, 2H), 7.66–7.60 (m, 2H), 7.25 (t, J=8.4 Hz, 2H), 7.18 (t, J=8.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 166.51, 164.64, 164.42, 163.80, 163.15, 161.35, 143.50 135.92, 135.88, 129.27, 129.15, 128.85, 128.74, 127.54, 127.41, 122.61, 120.32, 120.28, 116.58, 116.28, 116.08, 115.80. ESI-MS: m/z 335.64 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{20}H_{12}F_2N_2O$, 357.0810; found, 357.0802.

2-(4-Biphenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole (**IIId**) was obtained as a white solid. Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$): 8.26–8.13 (m, 4H), 7.76 (d, J=8.0 Hz, 2H), 7.66 (d, J=7.6 Hz, 2H), 7.49 (t, J=7.6 Hz, 2H), 7.41 (t, J=7.2 Hz, 1H), 7.23 (t, J=8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 166.47, 164.49, 163.73, 163.12, 144.49, 139.72, 129.25, 129.13, 128.98, 128.20, 127.66, 127.34, 127.12, 122.56, 120.35, 120.30, 116.55, 116.25. ESI-MS: m/z: 315.25 $[M+H]^+$. HRMS: $[M+Na]^+$ calculated for $C_{20}H_{13}FN_2O$, 339.0904; found, 339.0901.

4. Conclusion

A new series of 2,5-diaryl-1,3,4-oxadiazole derivatives without flexible chains were synthesised in good yields according to the Suzuki cross-coupling reaction. The liquid crystalline properties of these compounds are determined by the polarity, steric factors and positions of the terminal groups. The methoxy and methylthio groups are more beneficial to form stable mesophase than the terminal fluorine atom, whereas compounds with a hydrogen atom as one of the two terminal groups do not exhibit liquid crystalline behaviour.

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