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Mesogenic heterocyclic pyrazoles, isoxazoles and 1,3,4-oxadiazoles

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Three new series of liquid crystals **1-3** derived from heterocyclic pyrazoles, isoxazoles and 1,3,4-oxadiazoles exhibiting smectic A or C phases were reported. Compound **1a** exhibited monotropic smectic A phase, while the other two compounds **2-3a** were not mesogenic. In contrast, all other compounds **1-3b** bearing longer alkoxy chains exhibited smectic X and C phases, which were confirmed by powder XRD diffractometer. The clearing temperatures decreased in the order of compounds **1b** > **2b** > **3b**, in contrast the temperature range of smectic C phases increased in the order of compounds **1b** < **2b** < **3b**. The smectic phases in **1-3b** were formed by a monomeric structure, confirmed and consistent with powder X-ray diffraction data. The formation of mesomorphic behavior might be probably attributed to their exocyclic angles and/or H-bonds. All derivatives showed good stabilities at temperature below T = 346 °C on TGA analysis.

1. Introduction

Five-member rings, such as 1,3,4-oxadiazoles, pyrazoles and isoxazole considered as an important member among heterocyclic family have demonstrated many unique properties in the area of materials chemistry.[1–3] When appropriately designed, their structures were highly or/and extended conjugate, and some interesting or novel physicochemical and mechanical properties were obtained. Most heterocycles were often considered as electron deficient moieties. Incorporation of electronegativity atoms (N, O and S) into such electron-deficient moieties led to intrinsic or inherent dipoles compared to other all carbon homologues. On the other hand, these dipoles were easily polarized and might be intermolecularly induced by donor–acceptor, giving interesting mesogenic behavior.

The first mesogenic heterocyclic pyrazoles[4] **Ia** was reported in 1992. Since then, other five-membered heterocyclic isoxazoles[5] **Ib**, and 1,3,4-oxadiazoles[6] **Ic-Ie,** were prepared and their mesomorphism was investigated. These examples included monoheterocyclic **Ia-e** and bisheterocyclic rings[7] **IIa-d**. Most of them exhibited mesogenic behavior; nematic or/and smectic phases were observed depending on the molecular structures. Examples exhibiting columnar heterocyclic compounds were relatively rare. The weak π–π interaction, CH-π or/and H-bonding were often attributed to the formation of resulting mesomorphic behavior in such heterocyclic systems. In some of these systems, a quinoxaline **Ie**[8] or naphthalenyl moiety **Id**[6b,9] was incorporated to enhance the intermolecular interactions, and mesogenic behavior was greatly improved. The π-π interactions between the neighboring molecules were increased, which might probably favor the molecules to be arranged within the layers or columns. Among them, pyrazoles were particularly interesting due to their –NH bonds. Mesogenic pyrazoles often exhibited higher clearing temperatures and a wider temperature of mesophases than those of the other two heterocycles. On the other hands, the formation of mesophases was found to be also determined or/and controlled by their exocyclic angles. The effect of non-linear shapes, caused by a smaller exocyclic angle[10] (ε~134°, ~151–157° and ~159° for 1,3,4-oxadiazole, pyrazoles and isoxazole) also played an important key factor in generating mesophases. In general, the more linear geometry favored the formation of mesophases, whereas, the more pronounced bent shapes proved detrimental to the liquid crystalline phases.

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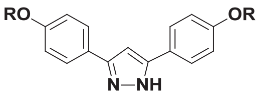

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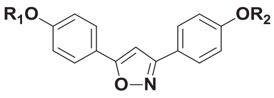

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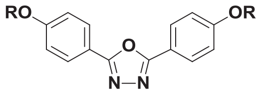
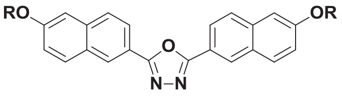


Ic



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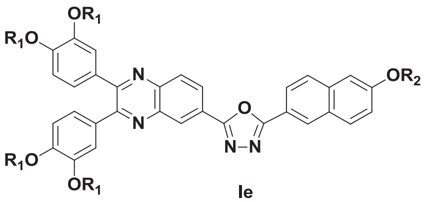

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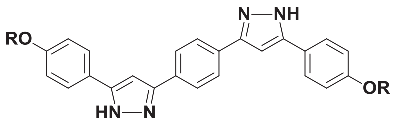
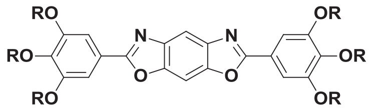


IIa



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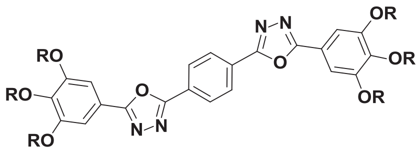
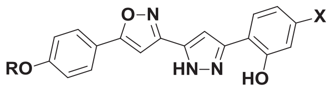


IIc



IId

In this work, three new series of unsymmetric Schiff bases derived from pyrazoles, isoxazoles and 1,3,4-oxadiazoles were prepared, characterized and their mesomorphic properties studied, as extended from our continuous studies in mesogenic heterocyclic compounds. Except for compounds **2-3a**, all other compounds **1a** and **1**-**3b** bearing longer alkoxy chains exhibited smectic A or C phases. The pyrazoles **1b** has the highest clearing temperatures than those of the other two compounds **2**-**3b**; in the order of compounds **1b** > **2b** > **3b**. The structures of mesophases in **1**-**3b** were also confirmed by powder X-ray diffraction data. The formation of mesomorphic behavior might be probably attributed to their exocyclic angles and/or H-bonds.

2. Results and discussions

2.1. Synthesis and characterization

The synthetic pathways used to prepare final heterocyclic compounds **1**–**3** are listed in Scheme 1. The procedures to prepare ethyl 4-(4-dodecyloxyphenyl)-2,4-dioxobutanoate in Scheme 1 was followed by our previous procedures. Two ethyl carboxylates; ethyl 5-(4-(dodecyloxy) phenyl)-1H-pyrazole-3-carboxylate and ethyl 5-(4-(dodecyloxy)phenyl)isoxazole-3-carboxylate were similarly prepared by the reactions of ethyl 4-(4-(dodecyloxy) phenyl)-2,4-dioxobutanoate and hydrazine monohydrate or hydroxylamine hydrochloride, respectively, with drops of acetic acid added in refluxing THF. The products, isolated as white solids were obtained after recrystallization from THF/MeOH or CH_2Cl_2/MeOH. On the other hand, ethyl 5-(4-(dodecyloxy) phenyl)-1,3,4-oxadiazole-2-carboxylate was obtained from the reaction of ethyl 2-(2-(4- (dodecyloxy)benzoyl)hydrazinyl)-2-oxoacetate in refluxing $SOCl_2$. The yellow products were obtained after recrystallization from THF/MeOH. The further reactions of these three ethyl carboxylates with hydrazine monohydrate in refluxing THF/EtOH led to the formation of isoxazole-3-carbohydrazide, pyrazole-3-carbohydrazide and 1,3,4-oxadiazole-2-carbohydrazide.

Another interesting synthetic procedure to 2,5-substituted 1,3,4-oxaziazoles[11] was also reported. All these intermediates were characterized by ^1H NMR and ^{13}C NMR spectroscopy. On the ^1H NMR spectrum, a characteristic peak appeared at δ 4.40, 4.62 and 4.81 ppm assigned for $-OCNHN\underline{H_2}$ was confirmed for the formation of the hydrides. The final Schiff bases **1**–**3** were obtained by the condensation of the three 3-carbohydrazides with appropriate 4-alkoxy benzaldehydes or benzaldehyde in refluxing THF/ethanol. All compounds **1**–**3**, isolated as white solids were obtained after twice recrystallization from THF/MeOH. The ^1H NMR and ^{13}C NMR spectra of all compounds **1b** were not obtained due to their poor solubility, and this poor solubility for compounds **1b** were observed in our previous pyrazolic systems. Mass spectroscopy and elemental analysis were also performed to confirm their structures. All characteristic peaks assigned for various functional groups in compounds **2**-**3b** are listed in Table 1.

In order to identify the formation of H-bonds possibly formed in crystal, liquid crystal or/and isotropic states, variable temperature FT-IR spectra of three heterocyclic compounds **1b**-**3b** (all $n = 12$) were performed. In this experiment, a thin disc grounded with KBr was prepared and studied at different temperatures on the heating process. On the FT-IR spectra (Fig. 1), two characteristic peaks assigned for functional groups of amide-NH and pyrazolic-NH were observed at 3270–3275 and 3085–3200 cm^{-1}. In contrast, the