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Polarization effects in mesogenic isoxazoles and 1,3,4-oxadiazoles

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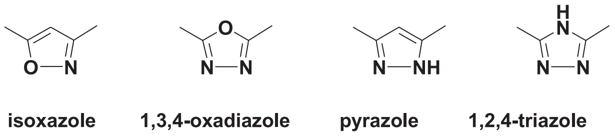
ABSTRACT

Four new series of unsymmetric isoxazoles and 1,3,4-oxadiazoles were prepared, characterized and their mesomorphic properties investigated. Isoxazoles were obtained by condensation–cyclization of β-diketones with hydroxylamine hydrochloride in refluxing THF, while 1,3,4-oxadiazoles were obtained from hydrazine-carboxylate in refluxing $POCl_3$. Two single crystallographic structures were determined by X-ray crystallographic analysis. A correlated dimeric structure was formed by H-bonds in isoxazoles **1a** (n=6), leading to a more elongated structure required for the formation of mesophases. All compounds **1a**–**c** formed N, SmA or/and SmC phases. In contrast, compounds **1d** exhibited columnar phases, and an N_{cell}=14.6 obtained from powder XRD data indicated that a correlated structure formed by four molecules was probably induced in Col_h phases. The better mesomorphic behavior formed in **1a** than **1b** might be attributed to stronger intermolecular interactions and higher polarization induced in isoxazoles **1a**.

1. Introduction

Isoxazoles, 1,3,4-oxadiazoles, pyrazoles, and 1,2,4-triazoles (Scheme 1) are in fact considered as the most few important heterocycles among numerous five-membered families. These heterocycles are also recognized as electron-deficient natures and good electron acceptors,[1] which lead them to be excellent candidates used in many potential applications as organic and bio-active materials.[2–9] All these heterocycles were incorporated or constituted with different atoms, such as carbon, oxygen or/and nitrogen. Heterocycles have different chemical or/and physical properties from all carbon rings due to different atoms incorporated, for example, sizes, dipole, electro-negativities, polarizability, etc. Electronegativity is defined as the ability of an atom in a molecule to attract shared electron to itself; the more difference between atoms, the more polar a bond will be. On the other hand, polarizability is the relative tendency of a charge distribution, like the electron cloud of an atom or molecule, to be distorted from its normal shape by an external electric field. A larger atom with many electrons often exhibited a higher polarizability than small atoms, thus the importance of London dispersion forces greatly increases as atomic size increases. Polarization abilities inherent from heterocyclic atoms; N, C or O atoms might electronically impart the overall structural flexibility and physical behavior. This is particularly important on the formation of mesogenic structures.



Scheme 1. Molecular structures of some known heterocyclic five-membered derivatives.

All these heterocycles are chemically and thermally stable. Interest in studying such highly π-conjugated liquid crystals containing heterocycles had enormously increased in the past decades.[10–15] Modern advanced synthetic techniques allowed chemists to access tailor-made materials with predictable properties. Some of them have been extensively studied in the areas of biochemistry and material chemistry. Examples containing all these four heterocycles as mesogenic rigid cores were known (Scheme 2). The formation of mesomorphic properties in such heterocyclic cores was believed to be attributed to their unsaturation and/or greater polarizability. Lower symmetries and/or nonplanar structures resulted from N, O, S or other atoms also favored giving mesophases with lower temperatures. The effect of non-linear shapes, caused by a larger exocyclic angle ($\varepsilon \sim 134°$,

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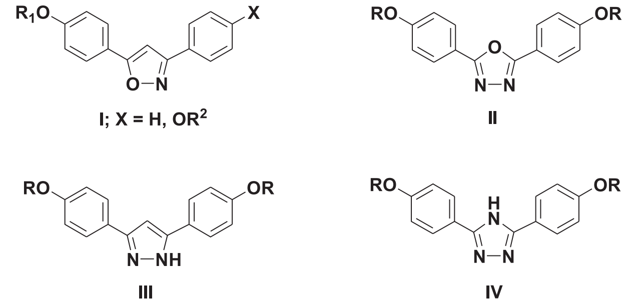


Scheme 2. Some of the known mesogenic examples of isoxazoles **I**, 1,3,4-oxadiazoles **II**, pyrazoles **III**, and 1,2,4-triazoles **IV**.

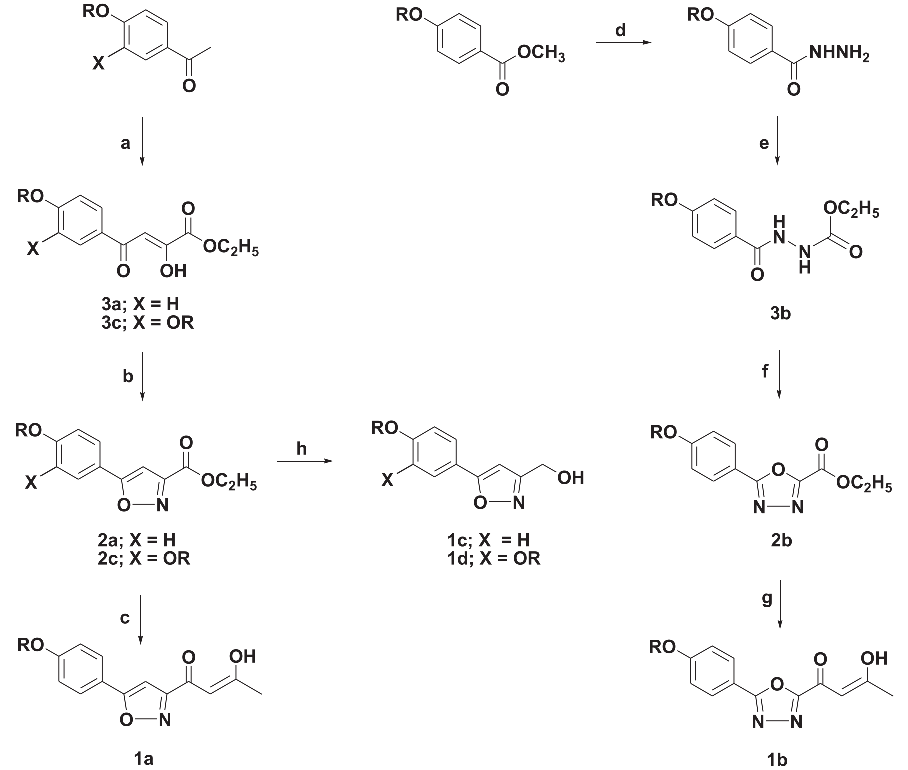
151–157°, 159° for 1,3,4-oxadiazole, pyrazole, isoxazole)[14,16–18] also played an important key factor in generating mesophases. In general, the more linear geometry favored the appearance of mesophases, whereas, the more pronounced bent shapes proved detrimental to the liquid crystalline phases. Few examples of 1,3,4-oxadiazoles formed interesting biaxial nematic phases (N_b).

In this work, four new series of unsymmetrical isoxazoles and 1,3,4-oxadiazoles were prepared, characterized and their mesomorphic properties studied, as extended from our previous studied in mesogenic heterocyclic isoxazoles[13] and 1,3,4-oxadiazoles.[19] A terminal moiety containing an α,β-unsaturated 1,3-dione was incorporated to enhance its dipole, as well as to keep their shapes as more linear. The 1,3-dione core is more bent shape due to its exocylic angle of $\varepsilon \sim 128°$. Their synthetic chemistries were well known and straightforward. A possible correlation between molecular structures and molecular arrangements deduced from two resolved single crystallographic data of two single crystals **1a** (n=6) and **1c** (n=14) were also discussed. The intermolecular H-bonds and π–π interactions were responsible to the formation of mesophases. All compounds **1a–c** formed N, SmA or/and SmC phases. In contrast, compounds **1d** exhibited columnar phases.

2. Results and discussion

2.1. Synthesis and characterization

The synthetic routes used in this work to prepare compounds **1a–d** are listed in Scheme 3. The preparations of α,β-diketones **3a** and **3c**, isolated as light yellow solids were easily followed by literature procedures. The isoxazoles **2a** and **2c** were prepared by condensation–cyclization of α,β-diketones **3a** and **3c** with hydroxylamine hydrochloride in refluxing THF/ethanol. The white compounds **1c,d** were obtained by reduction reactions of LAH at 0 °C in THF. The preparation of final isoxazoles **1a**, isolated as white solids were similar to procedures used to prepare compounds **3a** and **3c**. On the other hand, compounds **2b** were prepared by condensation reactions of ethyl 2-(4-(alkoxy)benzoyl)hydrazine-carboxylates **3b** through refluxing in $POCl_3$. The final compounds **1b** were obtained from compounds **2b** and acetone and NaH in refluxing THF. All these compounds were characterized by ^1H NMR and ^{13}C NMR spectroscopy, mass spectroscopy, and elemental analysis. The ^1H NMR spectra of all compounds **1**–**3** showed a few characteristic signals due to their features of keto–enol forms in chloroform-d solution, listed in Table 1. The elemental analyses of all compounds **1a**–**d** were all performed to confirm their purities.



Scheme 3. Reactions and reagents: (a) NaOEt (3.0 equiv), diethyl oxalate (2.0 equiv), stirred in dry THF at 0 °C, 2 h, 87%; (b) hydroxylamine hydrochloride (3.0 equiv), refluxing in THF/ethanol, 6 h, 71%; (c) dry acetone (2.0 equiv), NaH (3.0 equiv), refluxing in dry THF, 3 h, 45%; (d) hydrazine monohydrate (3.0 equiv), refluxing in ethanol, 36 h, 75%; (e) ethyl 2-chloro-2-oxoacetate (1.1 equiv), stirring in dry THF, 12 h, 80%; (f) refluxing in $POCl_3$, 24 h, 48%; (g) acetone (2.0 equiv), NaH (3.0 equiv), refluxing in dry THF, 3 h, 23%; (h) LAH (3.0 equiv), stirred at 0 °C in dry THF, 6 h, 70%.

2.2. Single crystal structures of (*Z*)-1-(5-(4-(hexyloxy)phenyl)isoxazol-3-yl)-3-hydroxybut-2-en-1-one 1a (n=6) and (5-(4-(tetradecyloxy)phenyl)isoxazol-3-yl)methanol 1c (n=14)

In order to understand the possible correlation between the molecular structures and mesomorphic behavior, two single