Columnar Mesomorphism of half-disc shaped molecules containing 1,2,4-oxadiazole

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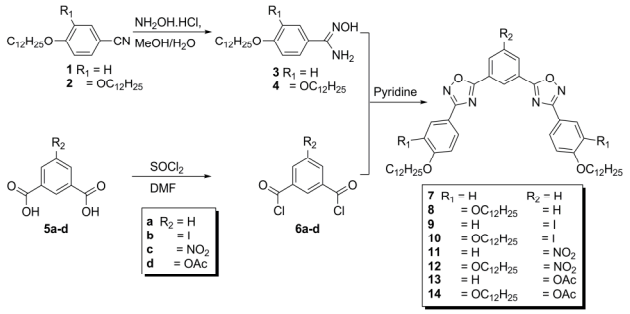
INTRODUCTION

Discotic liquid crystals (DLCs) are of great interest because of both their unique self-assembled structures[1] and their potential applications in organic devices such as field-effect transistors and photovoltaic solar cells, due to the high charge-carrier mobility along their one-dimensional (1D) aromatic π-π stacking.[2] Derivatives of 1,2,4-oxadiazoles have potential for application in advanced materials, as they present large dipole moments, charge-transport abilities besides blue fluorescence. However, such compounds have not been studied extensively in terms of their material properties.[3] In this work, the synthesis of some half-disc shaped molecules containing 1,2,4-oxadiazole and the study regarding the relationship between chemical structure and mesomorphic behavior, thermal and optical properties is reported.

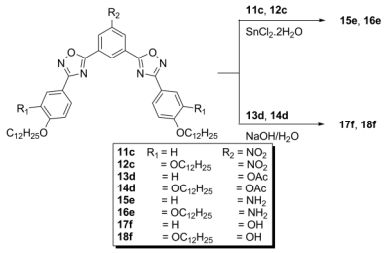
RESULTS AND DISCUSSION

Firstly, the 1,2,4-oxadiazole **7-14** starting from nitriles **1** and **2** and hydroxylamine hydrochloride were synthesized by Tiemann reaction[4] to afford the amidoximes **3** and **4**. The reaction between **3** or **4** and the freshly prepared acid dichloride **6a-d** in dry pyridine under reflux, afforded the final compounds **7**-**12** in 34-49 % (Scheme 1).



Scheme 1. Synthesis of compounds **7-14**.

The compounds **13d** and **14d** were not isolated, and the deprotection was performed, *in situ*, with $NaOH_{aq}$, resulting the compounds **17f** and **18f** in 62 and 59 % yields, respectively(Scheme 2). The compounds **15e** and **16e** were prepared from **11c** and **12c** *via* reduction of nitro group by $SnCl_2$, in yield of 93 and 90 %, respectively.



Scheme 2. Synthesis of final products **15-18**.

The structures of all the compounds were characterized by IR and ^1H and ^{13}C NMR spectra and elemental analysis. The mesomorphic properties of the final compounds were investigated by POM, DSC, and TGA. The mesophase were characterized by POM and DSC as a discotic hexagonal columnar phase (Col_h) for the compounds **8a**, **16e, 17f** and **18f** which were confirmed by XRD analysis. The photophysical properties of final compounds, in solution and in solid state, were evaluated, showing an weak blue emission in solution and with large Stoke shift (85-189 nm). All of the compounds presented good thermal stability with decomposition temperature ranging between 298 and 339 °C.

CONCLUSION

The design and synthesis of a new class of 1,2,4-oxadiazole heterocycles as a potential liquid crystals were reported in this work. Four of the ten molecules are liquid crystals. Their ability to form Col_h, despite their half-disc shape may be explained by the formation of antiparallel arrangement, which have been also observed by XRD analysis.

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