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Substituent and intramolecular hydrogen-bond effect on the fluorescent emission of two easy-synthesizable fused rigid bicyclic octadiene derivatives

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ABSTRACT

Tetra-*tert*-butyl-*cis,cis*-3,7-dihydroxybicyclo[3.3.0]octa-2,6-diene-2,4-*exo*-6,8-*exo*-tetracarboxylate (**I**) and tetra-*tert*-butyl-*cis,cis*-3,7-dimethoxybicyclo[3.3.0]octa-2,6-diene-2,4-*exo*-6,8-*exo*-tetracarboxylate (**II**) were prepared in a three step synthetic procedure. These compounds show two central five carbon atom rings, fused in such a way to define a central bicyclo[3.3.0]octa-2,6-diene core. The carbon atoms which fuse both rings have sp^3 hybridization, then they are not coplanar. A dihedral angle of about 63° corresponds to butterfly conformation. UV–Vis spectra of **I** and **II** measured in solution show symmetrical bands centred around 245 nm ($\varepsilon \sim 10^4$ $M^{-1}cm^{-1}$). These bands are consistent with $\pi\rightarrow\pi^*$ transitions. TD-DFT simulated spectra over the DFT optimized in gas phase confirms this hypothesis, and additionally suggest a non-negligible contribution of $n\rightarrow\pi^*$ transition for **II**. The slight dependence of λ_{max} on solvent polarity experimentally observed for **II** is consistent with some $n\pi^*$ character. After excitation at 250 nm, a weak emission around 400 nm was detected for both compounds, with quantum yield values below detection limit for **I**. The value of λ_{em} of **II** was observed to be sensible to the solvent polarity, confirming some relevant $n\rightarrow\pi^*$ character. The almost fully quenching of the emission of **I** in solution would be attributed to a rather strong intramolecular hydrogen bond established between the hydroxyl group and the oxo-oxygen atom from tert-butoxy group, which is observed in the crystal structure of the compound (O···O ranges from 2.635(2) Å to 2.672(2) Å). We hypothesize that it is probably preserved in solution due to the molecular rigidity, and would be the responsible for the quenching of the emission in solvent solution.

1. Introduction

Fused bicyclic rings are useful frameworks with several synthetic applications, using them as synthons, bridged cores or building block systems [1–4]. Interesting optical properties or photochemistry reactions have focused attention on these systems [5–9]. In particular, bicyclo[3.3.0]octa-2,6-dienes are easily prepared by the reaction of α-diketones with 3-oxoglutarate esters, being valuable precursors for organic synthesis. The use of this family of molecules strongly depends on the possibility to functionalize them through nucleophilic substitution, by removing one the two-acidic protons located in the carbon bicycle with a strong base (i.e. sodium hydride) and the subsequent reaction with an alkyl or aryl halide. However, since there are two equivalent positions in the molecule, the control of the reaction is difficult, even at low temperatures, a mixture of products, which is hard or even impossible to separate, is obtained [10]. An elegant way to overcome this issue, is to take advantage of steric hindrance on the carboxylate substituents. Even though they are not directly involved in the reaction, the use of a big substituent allows driving the reaction to a single product, simplifying isolation and purification for the further steps of synthesis.

Although the wide use of them as a part of synthetic routes, rather a handful have been fully structurally characterized. The structure of the Vossen's salt $C_{16}H_{15}O_{10}Na$, prepared by the first

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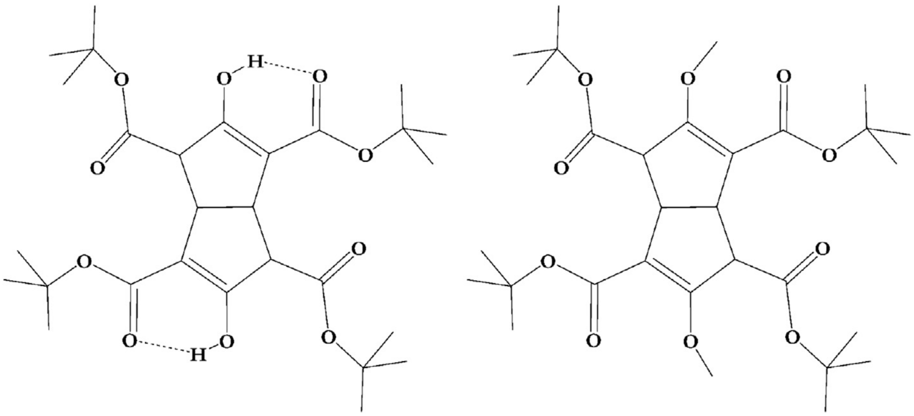
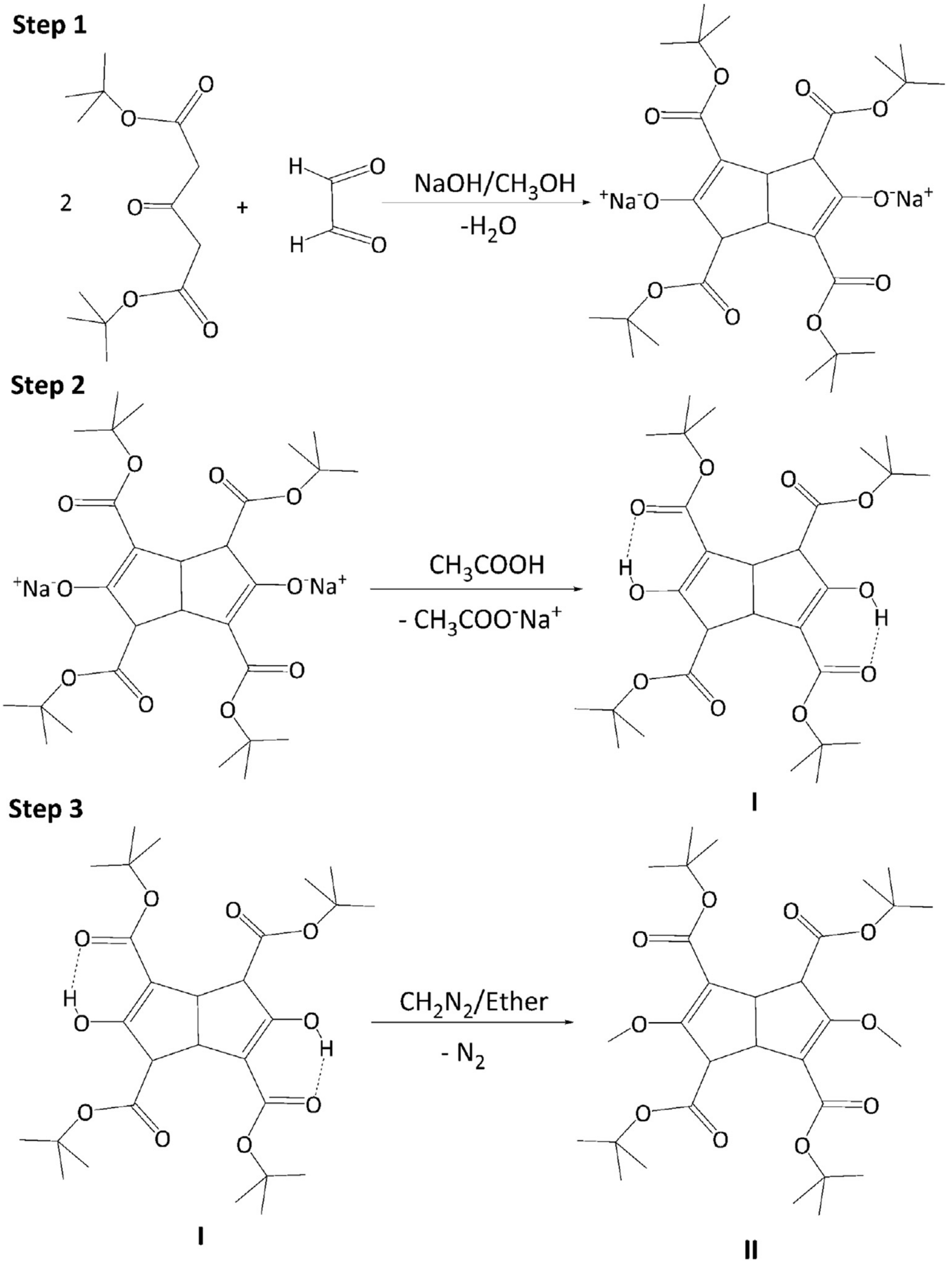


Scheme 1. Schematic view of **I** (*left*) and **II** (*right*).



Scheme 2. Synthetic path to **II.**