



Directed lithiation of a pyrene-1-carboxamide as a route to new pyrenyl fluorophores



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ABSTRACT

The lithiation of *N-tert*-butylpyrene-1-carboxamide with *n*BuLi-TMEDA in THF at -78 °C afforded, after quenching with chlorosilanes, the corresponding 2-(trialkylsilyl)pyrene-1-carboxamides. When DMF and diethyl oxalate were used as quenchers compounds having 8-*tert*-butyl-7-hydroxy-8,9-dihydro-7*H*-phenaleno-[1,9-*ef*]isoindole skeleton were obtained. The oxidation of compound having secondary OH group with Jones' reagent afforded 8-*tert*-butyl-7-hydroxy-8,9-dihydro-7*H*-phenaleno-[1,9-*ef*]isoindole-7,9(8*H*)dione. All of the synthesized compounds displayed fluorescence in solution ($\lambda_{\text{max}} = 425\text{--}451$ nm; $\Phi_{\text{F}} = 15.1\text{--}40.8\%$) and in the solid state ($\lambda_{\text{max}} = 410\text{--}555$ nm; $\Phi_{\text{F}} = 6\text{--}40\%$). The silylated amides display in the solid state monomer emission whereas in the case of the phenalenoisoindole derivatives the emitting species are π -stacked aggregates. The formation of aggregates in the crystals of the latter compounds was confirmed by a single-crystal X-ray diffraction study.

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1. Introduction

Pyrene and its derivatives are important and thoroughly investigated organic fluorophores for which many applications have been found in molecular electronics, photovoltaic cells and as fluorescent probes and sensors [1–4]. Considerable effort has been put into the development of synthetic methods leading to specifically substituted pyrenes [1,5]. We have recently disclosed an efficient synthesis of pyrene-1-carboxamides based on the Friedel-Crafts-type reaction of pyrene with isothiocyanates followed by oxidative desulfurization of the resulting thioamides with oxone[®] [6]. As was shown by Konishi et al. [7–10] and by us [6], pyrene-1-carboxamides display interesting luminescent properties in solution and in the solid state and therefore the search for simple and efficient methods enabling modification of this fluorophore by introducing additional substituents or functional groups is of obvious interest. It is now well established that carboxamido groups bound to aromatic or heteroaromatic rings facilitate lithiation of the *ortho* positions (directed lithiation) [11–16]. We

expected that this effect would be useful for modification of pyrene carboxamides and we report herein the preliminary results obtained for lithiation of *N-tert*-butylpyrene-1-carboxamide along with a study of the photophysical properties of the new pyrene amides obtained in this reaction.

2. Results and discussion

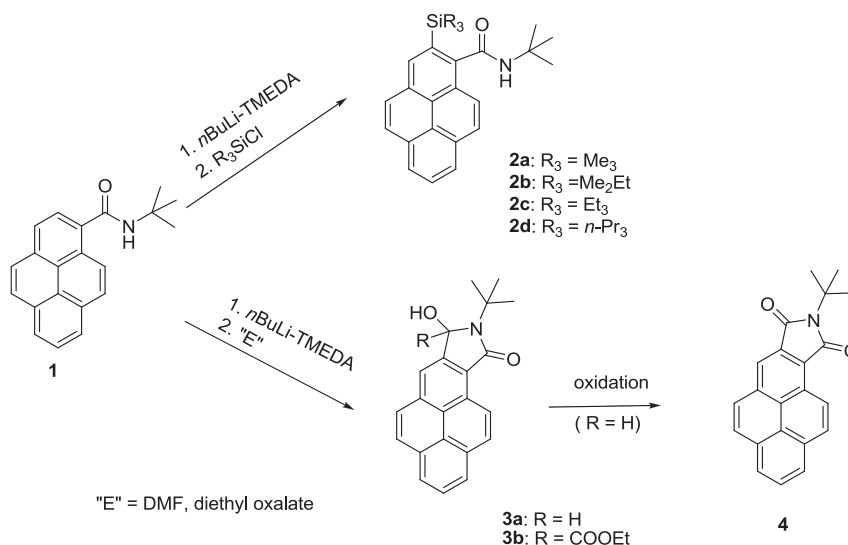
2.1. Directed lithiation

The performed reactions are shown in Scheme 1. In our first attempts we decided to use chlorosilanes as electrophilic quenchers because it is known that silyl groups enhance pyrene fluorescence due to $\sigma^*-\pi^*$ conjugation [17].

The amide **1** [6] treated with *n*BuLi (2 equiv.) and TMEDA (2 equiv.) in THF at -78 °C afforded, after quenching with various chlorosilanes, the corresponding 2-silylated amides **2a–c** in 58–73% yield. When DMF and diethyl oxalate were used as quenchers the heterocyclic amides **3a** and **3b** were isolated in 82% and 75% yield, respectively. The formation of the pyrrolidine ring in these compounds results from the addition of the amide N–H group to the carbonyl group introduced to the position 2 by the

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Scheme 1. Directed lithiation of **1**.

quencher. Finally, the oxidation of **3a** with Jones reagent afforded cyclic imide **4** in 95% yield. The substitution at C-2 not at C-4 (corresponding to the *peri*-position in naphthalene) was unambiguously determined by NMR spectra and by the crystal structures of **2a**, **3a–b**, and **4** (Fig. 1).

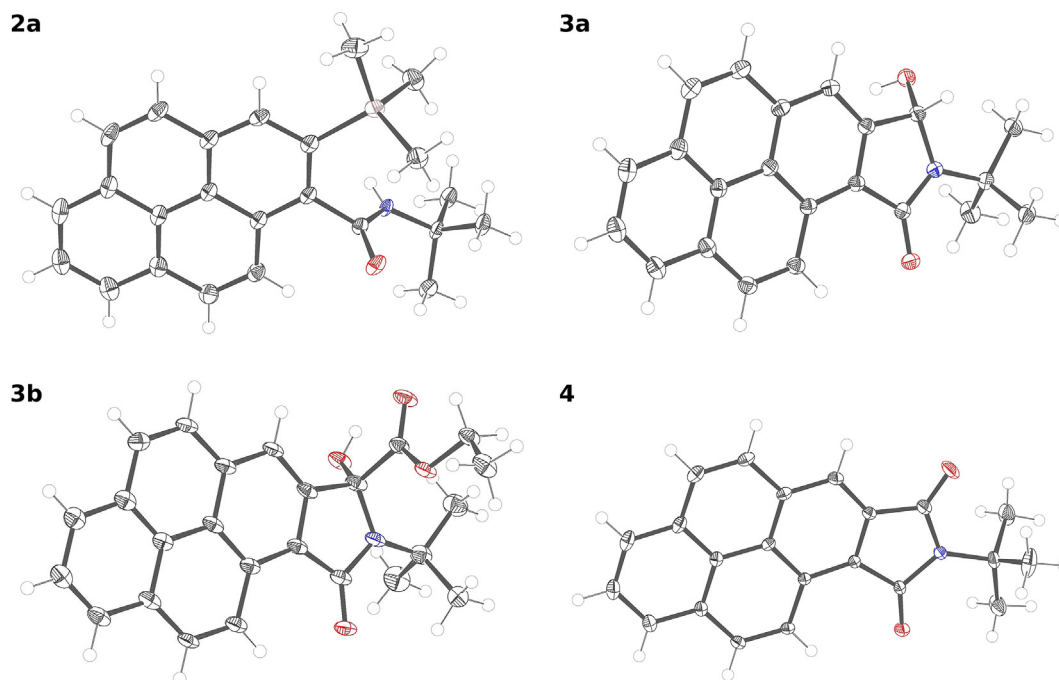
Although directed lithiation is now a powerful synthetic tool in the chemistry of aromatic and heteroaromatic compounds [11–16] it has so far found only a limited application in the synthesis of substituted pyrene derivatives, and reported examples are limited to the lithiation of 1-alkoxyppyrenes [18–20]. In our opinion, the results reported here reveal the synthetic potential of this approach for the synthesis of 1,2-disubstituted pyrenes.

All of the synthesized amides emit fluorescence in solution and in the solid state (Fig. 2).

2.2. Photophysical properties of **2a–d**, **3a–b** and **4** in solution

We have studied photophysical properties of the synthesized compounds in chloroform solution and in the solid-state. Although it has been found that some pyrenyl fluorophores undergo degradation upon illumination in this solvent [21], we did not observe such a phenomenon for **2a–d**, **3a–b** and **4**. Their absorption and emission spectra in chloroform solution and the emission spectra in the solid state (polycrystalline powders) are shown in Fig. 3 and the spectroscopic data are collected in Tables 1 and 2.

A comparison of electronic absorption and emission spectra of the synthesized compounds with those of **1** and pyrene (Fig. 4) measured in chloroform leads to the following conclusions. First, compounds **1** and **2a–d** display in chloroform the structured

Fig. 1. Crystal structures (ORTEP representations, 50% probability) of **2a**, **3a–b** and **4**.

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