Pyrene fluorophores bearing two carbonyl groups in 1,2- positions: Synthesis and photophysical properties of pyrene-1,2-dicarboximides and a pyrene-1,2-dicarboxamide

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ABSTRACT

Directed lithiation of pyrene-1-carboxamides, followed by reaction with DMF, afforded 7-hydroxy-8,9-dihydro-7H-phenaleno-[1,9-ef]isoindoles, which were oxidized with Jones reagent to the corresponding pyrene-1,2-dicarboximides. Similarly, the reaction of lithiated N-tert-butylpyrene-1-carboxamide with tert-butyl isocyanate afforded N,N'-di-tert-butylpyrene-1,2-dicarboxamide. The electronic structure and photophysical properties of these compounds were studied by means of theoretical (TD DFT) calculations and experimental (steady-state and time-resolved fluorescence) methods and were compared with those of their pyrene-1- monocarbonyl counterparts. The obtained results reveal the considerable influence of the carbonyl group at the 2-position on the structure and luminescent properties of this class of pyrenyl fluorophores.

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1. Introduction

Pyrene derivatives constitute a class of attractive and thoroughly investigated fluorophores for which numerous applications have been found in organic optoelectronics [1–4] and biology [5–8]. Special attention has been paid to carbonyl derivatives, which display environment-dependent fluorescence, resulting from the interplay between emissive $\pi\pi^*$ and non-emissive $n\pi^*$ excited states [9–17]. Most of the data concern synthetically readily available pyrene-1-carbonyl compounds. and there are only a few papers dealing with the photophysical properties of their 2-carbonyl analogues [18,19]. Furthermore, the data on pyrene derivatives bearing more than one carbonyl function are also scarce and limited to those on compounds substituted in 1–,3-,6- and 8- positions which are available via classical electrophilic substitution reactions of pyrene [20–22]. However, we recently reported the synthesis of a pyrene-1,2-dicarbonyl compound, N-tert-butyl-pyrene-1,2-dicarboxyimide, based on directed lithiation of N-tert-butylpyrene-1-carboxamide [23]. In this work we present the application of this methodology for the synthesis of a series of N-substituted pyrene-1,2-dicarboximides and a pyrene 1,2-dicarboxamide. We also studied the photophysical properties and electronic structure of these 1,2-dicarbonyl pyrene derivatives, which were compared to those of their 1-carbonyl counterparts. In our opinion, this study enables comparison of the perturbation of the pyrene π-system by electron withdrawing carbonyl groups in 1- and 2-position. It should be noted that it is believed that since both the HOMO and the LUMO of pyrene have nodal planes perpendicular to the molecular plane, which pass through the 2,7-positions, substituents at the 2-position are expected to exert less influence on the electronic properties of the pyrene moiety than those at the 1-position [24–26].

2. Results and discussion

2.1. Syntheses

We recently disclosed an efficient synthesis of imide 3c (Scheme 1) via reaction of lithiated amide 1c with N,N-dimethylformamide (DMF), followed by oxidation of the resulting 2c with Jones reagent [23]. In this work we applied this methodology for the synthesis of imides 3a,b,d which were isolated in 57–70% overall yield. Furthermore, the reaction of lithiated 1c with tert-butylisocyanate afforded diamide 4 in 65% yield.

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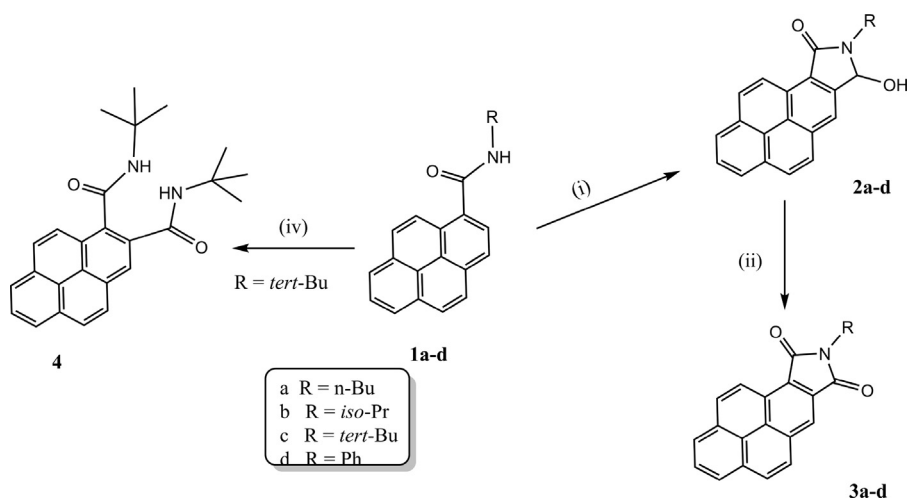
Scheme 1. (i): (a) *n*-BuLi-TMEDA,THF; (b) DMF. (ii): Jones reagent. (iv): (a) *n*-BuLi-TMEDA, THF; (b) *tert*-Bu-N=C=O.

2.2. Electronic absorption and emission spectra

We measured the electronic absorption and emission spectra of compounds **3a,b,d** and **4** in chloroform solution. Although photodecomposition of pyrene in this solvent has been reported [27], we found that this is not the case for the compounds studied here. To avoid excimer formation, spectra were recorded at low sample concentrations (10^{-6} mol dm^{-3}). The spectroscopic data along with those of compounds **1c, 3c** and **4** [23] are given in Table 1.

The selected spectra are presented in Fig. 1. The emission bands show vibronic structures and therefore can be assigned to excited fluorophore monomers.

In comparison to **1c**, compound **2c** shows red shift of the absorption (22 nm) and emission (4 nm) band, which was attributed to better electronic conjugation of the amido moiety with the pyrenyl group (the dihedral angle between these groups in the crystal of these compounds were 69∘ and 6∘, respectively). Oxidation of **2c** to **3c** was accompanied by a large bathochromic shift of the absorption and emission bands, thus indicating a considerable change in electronic structure due to the creation of the second carbonyl group at the 2-position.

We also determined fluorescence quantum yields of compounds under study. The obtained values (Table 1) are in the range of values reported for other pyrene-1-carbonyl compounds (e.g. >0.002 for 1-acetylpyrene, 0.63 for pyrene-1-carboxylic acid and 0.56 for its ester in dichloromethane)[28].

We also performed a time-resolved fluorescence study of the synthesized compounds in chloroform solution. We observed mono-exponential or bi-exponential fluorescence decays with the lifetimes shown in Table 1 along with the calculated corresponding radiative (k_r) and nonradiative rate constants (k_{nr}). The bi-exponential decays are characteristic for compounds having the *tert*-butyl group attached to the nitrogen atom. They suggest the presence of two emissive excited species, but so far their nature remains elusive.

Compounds **2c** shows approximately two times faster non-radiative excited state deactivation than amide **1c**, which brings about considerable decrease of the emission quantum yield of the former compound. Imides **3a–d** display faster radiative and slower nonradiative decays than **2c** leading to higher fluorescence quantum yields. Interestingly, imides bearing alkyl groups at the nitrogen atom show similar radiative constants (9.49-9.85×10^7 s^{-1}), whereas nonradiative constants increase with the ramification of these groups (*n*-Bu < isoPr < *tert*-Bu). Finally, comparison of the data of **3c** and **2c** shows considerable difference in radiative rate constants (9.85×10^7 s^{-1} and 2.98×10^7 s^{-1}, respectively), whereas nonradiative constants are closely similar (14.29×10^7 s^{-1} and 15.96×10^7 s^{-1}, respectively). The above discussion leads do conclusion that nitrogen substitution affects mainly nonradiative excited-state deactivation channel, whereas the radiative decays in this series of compounds are affected by the presence of the carbonyl function at the 2-position (compounds having this function have k_r in the range of ~9.5–11 $\times 10^7$ s^{-1} (with the exception for **4**), whereas the others ~3.0–3.8 10^7 s^{-1}, respectively). Therefore, the *N*-substituents presumably behave as molecular rotors, consuming excitation energy *via* rotational and vibrational movements [29].

To confirm this hypothesis we have determined emission quantum yields of **2c** and **3c** at room temperature in a viscous

Table 1
Photophysical data for compounds **1c**, **3a–d** and **4** in chloroform solution (c = 10^{-6} mol dm^{-3}).

Compound	Absorption λ_{max}(nm)	Emission λ_{max}(nm)	Φ_F	τ/ns (contribution)	k_r[a] 10^7 s^{-1}	k_{nr}[a] 10^7 s^{-1}
1c[b]	315, 329, 344, 377	382, 401, 422	0.30 ± 0.02	$8.38 \pm 0.8(0.83)$ $3.48 \pm 0.3\,(0.17)$	3.75	8.76
2c[b]	332, 348, 360, 366, 385	386, 408, 431	0.14 ± 0.02	$5.34 \pm 0.5\,(0.85)$; $2.60 \pm 0.3\,(0.15)$	2.98	15.96
3a	307, 321, 357, 373, 405, 427	460	0.52 ± 0.03	$5.48 \pm 0.5\,(1.00)$	9.49	8.76
3b	307, 321, 356, 372, 404, 427	457	0.49 ± 0.03	$5.16 \pm 0.5\,(1.00)$	9.50	9.88
3c[b]	305, 321, 356, 371, 401, 423	451	0.41 ± 0.03	$4.28 \pm 0.4\,(0.86)$; $2.91 \pm 0.3(0.14)$	9.85	14.29
3d	304, 320, 358, 373, 408, 431	461	0.50 ± 0.03	$4.49 \pm 0.4\,(1.00)$	11.14	11.14
4	302, 315, 327, 344, 385	392, 414, 437	0.39 ± 0.03	$17.2 \pm 1.7\,(1.00)$	2.27	3.55

[a] $k_r = \Phi_F/<\tau>$; $k_{nr} = (1-\Phi_F)/<\tau>$, where $<\tau> = (\alpha_1\tau_1^2 + \alpha_2\tau_2^2)/(\alpha_1\tau_1 + \alpha_2\tau_2)$; τ_i: decay times; α_i: pre-exponential factors.
[b] Data from reference [23].