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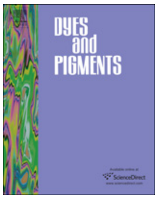

Boradipyrromethenecyanines derived from conformationally restricted nuclei

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ABSTRACT

A series of *meso*-polymethine-substituted 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes were synthesized based on the reaction of *meso*-methyl borondipyrromethene with a number of hemicyanine derivatives. The dyes obtained exhibited a weak short-wavelength absorption, a strong long-wavelength absorption and weak fluorescence. Upon protonation, the long-wavelength band disappeared while the intensity of the short-wavelength band increased markedly. The properties of the dyes were closely related to those merocyanine dyes rather than borondipyrromethenes.

1. Introduction

The dyes derived from borondipyrromethene (BODIPY) have attracted considerable attention over the past two decades on account of their excellent thermal, chemical and photochemical stability, high molar absorption coefficient, high fluorescence quantum yield, general insensitivity to solvent polarity and pH, large two-photon cross-section for multiphoton excitation, lack of ionic charge and good solubility [1–4]. However, most BODIPY compounds have absorption maxima below 600 nm. As long-wavelength dyes are important [5,6] there are many synthetic approaches for modifying the BODIPY system so as to red shift their absorption maxima.

One of the most promising approaches to the modification of BODIPY is its peripheral functionalization with conjugated chromophores. A wealth of studies have been devoted to the synthesis of α-substituted BODIPYs **A** [7–11] including derivatives **B** with dimethylamino auxochromes [12–17] (see Scheme 1). The styryl moieties at the α-positions cause a noticeable bathochromic shift in lambda max of the dye. Introduction of additional 4-dialkylamino substituents into **A** (structure **B**) results in even more pronounced spectral changes, with bathochromic shifts around 80 nm. Under acidic conditions only the diethylamino groups are protonated, leading to the optical properties that are very similar to those of **A**, where Ar = Ph. As known, in cyanine dyes the chain carbon atoms are the very positions which can be protonated, unlike terminal groups [18,19]. Therefore, in case of **B** dialkylamino groups cannot be referred to as true "end groups" as they are considered in the ideology of polymethine dyes. Thus, these NR_2 groups in structures **B** provide considerable spectral effects but do not change the nature of colour of the BODIPY core. Derivatives **C** *meso*-functionalized with *p*-dimethylaminophenyl groups [20–25] show much the same absorption as the unsubstituted BODIPY nucleus and, like **B** compounds, drastically reduced fluorescence.

We have recently established that *meso*-substitution of BODIPY with more complex heterocycle-terminated polymethine chains results in the formation of merocyanine dyes (see compounds **5a**–**7a** in Scheme 3) and thus qualitatively change the very nature of the BODIPY absorption [26]. These dyes are mainly characterized by two electronic transitions, one long-wavelength polymethinic and the other short-wavelength localized in the borondipyrromethene moiety. In terms of conventional cyanine nomenclature, we have introduced the term boradipyrromethenecyanines to describe these new substituted BODIPY systems.

The present work is directed towards the synthesis of dyes structurally similar to **5a**–**7a** and containing the bridged borondipyrromethene residue **4** as one end group. It is known that the bridging of α-aryl substituents causes significant bathochromic shifts in the absorption of BODIPYs as well as an increase in their molar absorption coefficients and fluorescence quantum yields [27,28]. Thus, our concern is with the effects caused by these structural changes on the spectra of the corresponding boradipyrromethene merocyanines.

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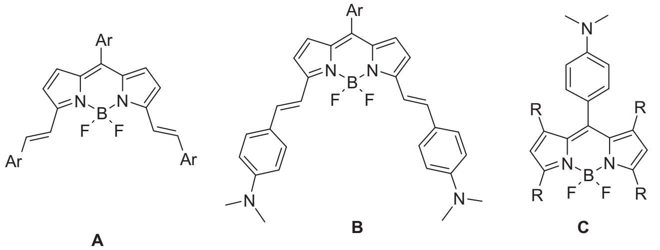


Scheme 1.

2. Results and discussion

Compound **4** was synthesized similarly to its analogue **4a** [26]. Pyrrole **1** [29] was condensed with triethyl orthoacetate in the presence of *p*-toluenesulfonic acid to give the tosylate salt of dipyrromethene **2** (see Scheme 2).

Unlike the previously described unbridged analogue [26], this salt appears to be quite stable in solutions; the ^{1}H NMR spectrum in DMSO-d_6 exhibits no signs of dissociation. One can therefore assume that the ethylene bridging of the dipyrromethene moiety makes this unit more basic. The absorption spectrum of **2** in dichloromethane likewise suggests its stability, whereas a significantly reduced molar absorption coefficient in more polar DMF points to the partial dissociation of the salt (see Table 1). When treated with triethylamine in ethanol, salt **2** is converted to compound **3** characterized by the ^{1}H NMR-detectable prototropic tautomerism of ethylene **3a** and *meso*-methyldipyrromethene form **3b**. The former is observed in highly polar DMSO-d_6, and the latter in weakly polar $CDCl_3$. Salt **2** was boiled in chloroform with boron trifluoride etherate in the presence of Hünig's base to produce **4** in high yield (90%); **4** is also obtainable from **3a** under the same conditions.

The *meso*-methyl group of compound **4** appears to be quite reactive in condensations with (2-acetanilidovinyl) heterocyclic derivatives (see Scheme 3). A series of dyes **5**–**8** containing, respectively, 2-indolenyl, 2-benzothiazolyl, 2-quinolyl, and 4-quinolyl as the second heterocyclic end residue (in the order of increasing basicity) were obtained. The corresponding cyanine condensations proceeded quite smoothly to furnish the dyes desired in good yields (45–65%). It should be noted that even dye **8** with the very basic 4-quinolyl end nucleus was prepared successfully, whereas its unbridged analogue proved inaccessible via the conventional procedure [26].

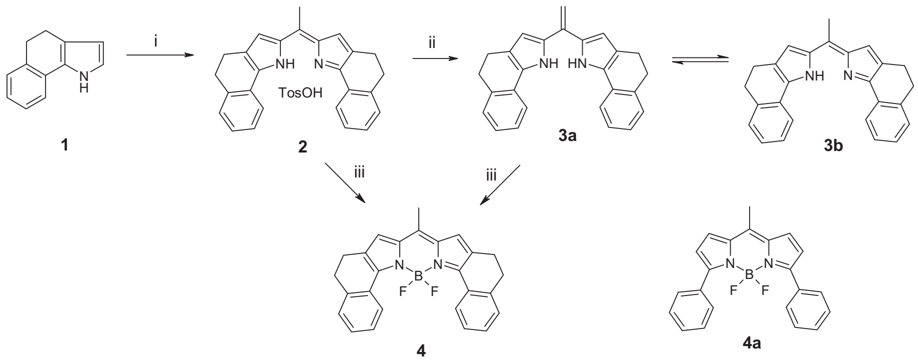
As expected, compound **4** is more deeply coloured than its unbridged counterpart **4a**; a noticeable batho- and hyper-chromic effect in absorption is accompanied by a significant increase in the fluorescence quantum yield (see Scheme 2). At the same time, the spectral properties of dyes **5**–**8** are much like those of analogous compounds **5a**–**7a** (see Fig. 1 and Table 1). They also exhibit two absorption bands: long-wavelength having the polymethinic origin and short-wavelength assigned to the electronic transition in the borondipyrromethene moiety. The latter is red-shifted due to bridging, so that the two bands are closer to each other than for dyes **5a**–**7a**. In DMF solutions, the absorption of merocyanines **5**–**7** is shifted only 20–33 nm to longer wavelengths and a little more intense relative to respective dyes **5a**–**7a** (see Table 1). This unexpectedly slight difference in spectral behaviour between bridged and unbridged dyes is attributable to the competition between the batho- and hyper-chromic effect of bridging, on the one hand, and the opposite trend caused by the less polymethinic character of the bridged dyes, on the other hand. Indeed, bridging makes the borondipyrromethene nucleus, as well as its boron-free precursor, less electron-withdrawing; at the same time, it is known that any decrease in the donor-acceptor strength of end groups brings the corresponding neutral merocyanines further from the so-called cyanine limit [30] and hence blue-shifts their absorption.

The borondipyrromethene local absorption peak which appears for indolenine dye **5** as a shoulder of the polymethinic band becomes increasingly separate for dyes **6**–**8** as the basicity of the second end group rises. The band separation is caused by an increasing red shift of the long-wavelength polymethinic absorption as a result of the approach to the cyanine limit with rising donor–acceptor difference of dye end groups. Accordingly, the long-wavelength and short-wavelength bands of dye **8** (much weaker than those of the other dyes in the series) are practically resolved from each other.

For all the dyes obtained, just as for their unbridged analogues **5a**–**7a**, protonation with strong acid results in a complete disappearance of the long-wavelength band and an intensity increase of the short-wavelength band. This effect is exemplified by the absorption of protonated dye **6** in Fig. 1.

As already mentioned, dipyrromethene **2** and hence its boron compound **4** are weaker electron-acceptors than their unbridged analogues. Accordingly, the ^{1}H NMR signal of the methyl group in compound **4** is shifted upfield from that in **4a** (cf. the respective chemical shifts of 2.64 and 2.76 ppm). Likewise, dyes **5**–**7** exhibit upfield shifts (of about 0.2 ppm) for the proton resonances of the polymethine chain in comparison to respective analogues **5a**–**7a**.

Solvatochromism of the merocyanines obtained is illustrated by the absorption of dye **5** which demonstrates batho- and



λ_{abs}= 621 nm (CH_2Cl_2)
ε = 134000, ϕ = 0.86

λ_{abs}= 544 nm (CH_2Cl_2)
ε = 57000, ϕ = 0.64

Scheme 2. Reagents: (i) $CH_3(OEt)_3$, TosOH·H_2O; (ii) Et_3N, EtOH; (iii) $BF_3 \cdot Et_2O$, Et(*i*-Pr)$_2$N.