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Azine-imidazole *aza*-BODIPY analogues with large Stokes shift

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ABSTRACT

A series of azine-imidazole *aza*-BODIPY analogues has been prepared by a simple synthesis from 2-azinecarboxylic acids and imidazole *N*-oxides. The new fluorescent complexes exhibit large Stokes shifts (up to 10 000 cm^{-1}), fluorescence in crystalline phase, high stability and fluorescence solvatochromism.

1. Introduction

Boron dipyrromethenes (BODIPYs) and their *aza* analogues have become one of the most important and useful classes of fluorescent dyes [1–5]. Apart from their excellent photophysical and chemical properties, important limitations of BODIPYs are (i) small Stokes shift values causing self absorption and interference with fluorescence measurements, (ii) aggregation-induced fluorescence quenching in the solid state. Therefore, a great research effort has been directed towards development of unsymmetrical BODIPY analogues, in which relaxation of molecular geometry in the excited state allows to achieve large Stokes shift [6], and stacking of π-conjugated chromophores one above another is avoided or diminished in condensed phase. A straightforward approach to this problem is desymmetrisation of the standard BODIPY core by appending donor and acceptor substituents [7–11] or condensation of aromatic rings to one of the pyrrole rings [12,13]. In recent years a rapidly developing area is construction of N-B-N and N-B-O complexes in which the boron atom is chelated by a nitrogen heterocycle and imido or imine nitrogen [14–21] or enolate/phenolate oxygen [22–28], or between two different heterocyclic systems other than pyrrole, with [29–37] or without [38–41] a bridging meso atom. Such complexes offer wide possibilities in terms of structural variation and often exhibit large Stokes shifts, particularly those incorporating an azine unit [29,32,35–37]. Efficient solid state fluorescence has been also reported for triazaborines [42] and di- and triazaanthracene BF_2 complexes, which can be considered BODIPY analogues containing two azine rings [43–48]. In particular, Kubota, Matsui and co-workers described a series of unsymmetrically substituted BF_2 pyridomethenes, which exhibited fluorescence in the solid state, even though the shift between absorption and fluorescence maxima was relatively small (up to 22 nm) [43]. The parent difluoroboron-triazaanthracene absorbs and emits in the blue region of the visible light spectrum and exhibits high lasing efficiency [44].

Herein we report that novel unsymmetrical BF_2 complexes **1** exhibiting very good optical properties, such us very high Stokes shift values and fluorescence in solid state, can be assembled in a straightforward manner from two types of very common heterocyclic systems, an azine (pyridine, quinoline, etc.) and an imidazole (Scheme 1). The chemistry of the derivatives of both types of heterocycles is very rich, which opens diverse possibilities of further functionalization of chromophores **1**.

Synthesis of complexes **1** requires preparation of unsymmetrical bis(heteroaryl)amine chelating ligands with appropriately placed imidazole and azine units. Bis(heteroaryl)amines are important as ligands [49–54] and pharmaceuticals [55] and a few general methods of their synthesis have been described: (i) nucleophilic

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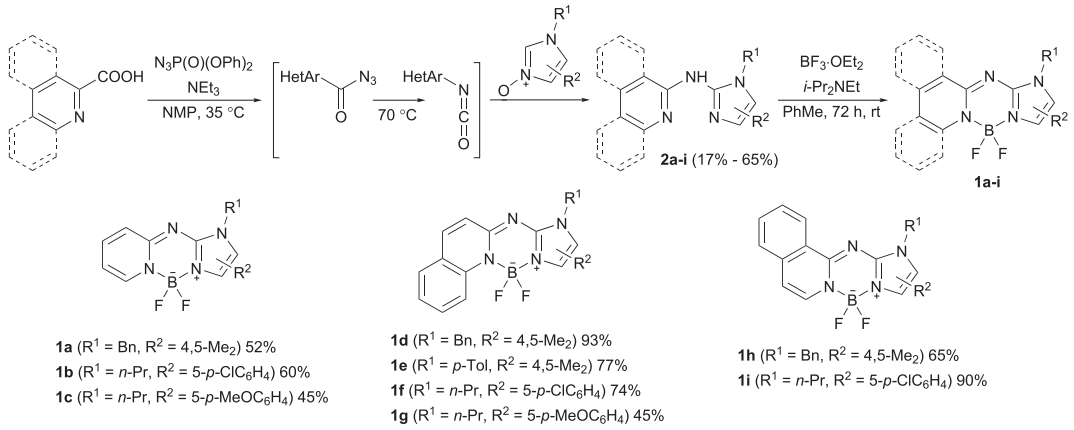

Scheme 1. Synthesis of azine-imidazole boron difluoride complexes.

aromatic substitution of halogen or hydrogen in azines with 2-aminoheterocycles [56–58] or *cine* substitution in *N*-oxides [59], (ii) Cu [60] or Pd-catalyzed [61–64] C–N bond formation, and (iii) assembly from acyclic precursors [65].

Considering the importance of bis(heteroaryl)amines and as a continuation of our studies on functionalisation of heteroaromatic rings by 1,3-dipolar cycloaddition of *N*-oxides of azines and azoles [66], we chose to investigate and develop cycloaddition between *N*-oxides and heteroaryl isocyanates as an alternative approach to constructing the requisite bis(heteroaryl)amine ligands **2** in a flexible manner from readily available substrates and without the use of transition metal catalysis.

2. Experimental

2.1. Materials and instruments

Analytical grade solvents were used as received. Hexanes used for extraction and chromatography were distilled before use. Commercially available dry NMP (Aldrich) was used for cycloaddition reactions. Flash chromatography was performed using silica gel 60 (0.040–0.063 mm). Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plates (Merck, 0.20 mm thickness) and visualized under a UV lamp. NMR spectra were recorded at 25 °C in $CDCl_3$ at the spectrometer frequency indicated in the description of each compound, using Bruker 400 and Varian 500 spectrometers. Chemical shifts are given in ppm relative to TMS for ^1H and ^{13}C NMR spectra and $CFCl_3$ for ^{19}F NMR spectra. Mass spectra were obtained using electron impact (EI) ionisation (Waters AutoSpec Premier) or electrospray (ESI) ionisation (Waters MaldiSYNAPT G2-S HDMS). IR spectra were obtained using a Perkin-Elmer 1640 FT-IR spectrometer. Elemental analysis was performed on a Perkin-Elmer 240 Elemental Analyzer (C, H, N) or using Schöniger method (titration with $Th(NO_3)_4$; F).

Heteroarylcarboxylic acids (2-pyridyl, 2-quinolinyl and 1-isoquinolinyl) are commercially available and were used as received. Preparation and characterization of imidazole *N*-oxides has been reported by us recently [66]. 1-Benzyl-4,5-dimethylimidazole 3-oxide was prepared according to a literature procedure [67]. 4,5-Dimethyl-1-*p*-tolylimidazole 3-oxide was prepared from 1,3,5-tris(*p*-tolyl)hexahydro-*sym*-triazine [68]. 5-(4-Chlorophenyl)-1-*n*-propylimidazole 3-oxide and 5-(4-methoxyphenyl)-1-*n*-propylimidazole 3-oxide were obtained from the corresponding a-ketooximes [69] using cyclisation method described in the literature [70].

2.2. Synthesis and characterisation

2.2.1. General procedure for preparation of bis(heteroaryl)amines **2**

2-Pyridinecarboxylic, 2-quinolinecarboxylic or 1-isoquinolinecarboxylic acid (1.5 mmol) and NEt_3 (1.5 mmol, 152 mg, 209 μL) were added to dry NMP (2.1 mL) in a Schlenk flask under Ar atmosphere. At 0 °C, diphenyl phosphoryl azide (1.6 mmol, 440 mg, 345 μL) was added drop-wise and the reaction mixture was stirred at 35 °C for 1 h. *N*-Oxide (1 mmol) was then added in one portion and the reaction mixture was stirred at 70 °C for 20 h. The mixture was then poured into water (50 mL) and extracted with AcOEt (3 × 20 mL). Combined organic extracts were washed with brine (5 × 30 mL) dried over anhyd. Na_2SO_4 and evaporated. Products **2** were purified by column chromatography on silica gel using hexanes–AcOEt 2:1 or toluene–AcOEt 2:1, then AcOEt as eluent.

*2.2.1.1. 1-Benzyl-4,5-dimethyl-2-(2-pyridylamino)imidazole (**2a**).* Obtained in 148 mg (53%) yield as yellow oil. IR (CH_2Cl_2): ν_{max} = 3217, 3062, 3031, 2923, 2097, 1579, 1540, 1464, 1438, 1355, 1311, 1149, 775, 733, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.00 (3H, s), 2.14 (3H, s), 5.03 (2H, s), 6.59 (1H, t, $^3J_{HH}$ = 6.1 Hz), 6.95 (1H, d, $^3J_{HH}$ = 8.5 Hz), 7.07 (2H, d, $^3J_{HH}$ = 7.1 Hz), 7.25 (3H, m), 7.40 (1H, ddd, $^3J_{HH}$ = 8.7 Hz, 7.0 Hz, $^4J_{HH}$ = 1.8 Hz), 8.01 (1H, dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.1 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.9, 12.0, 46.1, 112.5, 114.0, 119.1, 126.4, 127.4, 128.7, 137.2, 137.3, 137.6, 143.2, 146.0, 157.5 ppm. HRMS (ESI) calcd for $C_{17}H_{19}N_4$ ($[M+H]^+$), 279.1610; found, 279.1605.

*2.2.1.2. 5-(4-Chlorophenyl)-1-n-propyl-2-(2-pyridylamino)imidazole (**2b**).* Obtained in 200 mg (64%) yield as yellow oil. IR (KBr): ν_{max} = 3217, 3037, 2968, 1694, 1592, 1549, 1515, 1471, 1440, 1319, 1161, 1136, 1089, 994, 963, 839, 810, 770, 618, 522 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.75 (3H, t, $^3J_{HH}$ = 7.4 Hz), 1.58 (2H, m, $^3J_{HH}$ = 7.5 Hz), 3.91 (2H, t, $^3J_{HH}$ = 7.5 Hz), 6.68 (1H, m), 6.90 (1H, s), 7.25 (1H, m), 7.32 (2H, dm, $^3J_{HH}$ = 8.5 Hz), 7.40 (2H, dm, $^3J_{HH}$ = 8.5 Hz), 7.49 (1H, t, $^3J_{HH}$ = 7.1 Hz), 8.02 (1H, m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.9, 23.3, 44.9, 112.6, 112.6, 114.5, 123.5, 129.0, 129.3, 129.7, 133.7, 137.9, 145.2, 145.2, 155.4 ppm. HRMS (ESI) calcd for $C_{17}H_{18}N_4Cl$ ($[M+H]^+$), 313.1220; found, 313.1216.

*2.2.1.3. 5-(4-Methoxyphenyl)-1-n-propyl-2-(2-pyridylamino)imidazole (**2c**).* Obtained in 107 mg (35%) yield as yellow oil. IR (CH_2Cl_2): ν_{max} = 3211, 2963, 1599, 1578, 1465, 1438, 1249, 1177, 1030, 836, 772 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.72 (3H, t, $^3J_{HH}$ = 7.4 Hz),