Dyes and Pigments 134 (2016) 618–632

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis of novel substituted methoxybenzo[2,3-*b*]carbazole derivatives via C-H functionalization. Experimental and theoretical characterization of their photophysical properties

Cinthia da Silva Lisboa, Nanci C. de Lucas, Simon J. Garden*

Instituto de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária CT bloco A, RJ 21941-909, Brazil

ARTICLE INFO

Article history:
Received 25 May 2016
Received in revised form
1 August 2016
Accepted 5 August 2016
Available online 7 August 2016

Keywords:
Palladium catalysis
Oxidative C–H functionalization
Benzo[2,3-*b*]carbazoles
UV–vis spectroscopy
Time resolved fluorescence spectroscopy
Density functional theory calculations

ABSTRACT

The novel, highly blue, fluorescent *N*-methyl-6,11-dimethoxybenzo[2,3-*b*]carbazole derivatives were prepared by oxidative coupling of anilines with naphthoquinone followed by palladium catalyzed oxidative C–H functionalization and a one pot reductive methylation reaction. The benzocarbazole fluorophores were photophysically characterized and the effects of the substituents investigated. (TD)-DFT calculations faithfully reproduced experimental photophysical properties of the benzocarbazoles and revealed how the substituents affect the photophysical properties of these compounds.

1. Introduction

Carbazole derivatives are an important class of nitrogen containing heterocyclic compounds that are widespread in nature and have been found to have useful applications. Since the isolation of carbazole in 1872 by Graebe and Glazer [1], and later the description of the isolation and antimicrobial properties of murrayanine, a naturally occurring carbazole alkaloid from *Murraya koenigii* Spreng [2], the intriguing structural features and promising pharmacological activities of these natural products have attracted the attention of numerous research groups. The interest in this heterocyclic system has led to the isolation of new natural compounds and an enormous effort to develop synthetic methodology for the synthesis of novel derivatives [3]. The carbazole structure is found in a wide range of compounds that possess a diverse array of pharmacological activities, including anti-tumor, antibacterial, anti-parasitic, antifungal, anti-inflammatory, and as treatments for neurological disorders [3a,3b,4].

In addition to the interesting pharmacological properties of carbazole derivatives, carbazole derivatives have been increasingly attracting attention in terms of their electrical and optical properties [5]. Applications of carbazole derivatives include for example: use in organic light emitting diodes,[5m,6] organic photorefractive materials [7], optical sensors [8], as an active semiconductor layer in organic field effect transistors [9], as a fluorescent switch [10], or as components of dye-sensitized solar cells.[6h,11]

The present study details the synthesis and photophysical characterization of novel 6,11-dimethoxybenzo[*b*]carbazole derivatives derived from benzocarbazol-6,11-diones [12] and comparison is made with the known properties of carbazole [13] and other derivatives of the parent heterocyclic system benzo[2,3-*b*] carbazole [13a,14].

2. Experimental section

2.1. General

All reagents were purchased from Sigma-Aldrich and used as received. Spectroscopic grade solvents were used for the photophysical characterization of the benzocarbazole derivatives. ^{1}H and ^{13}C NMR spectra were recorded using either a Bruker 200, 300 or 500 MHz spectrometer with TMS as an internal standard. Mass spectra (ESI:HRMS) were obtained with a Mass Spectrometer Q-

---

* Corresponding author.
E-mail address: garden@iq.ufrj.br (S.J. Garden).

http://dx.doi.org/10.1016/j.dyepig.2016.08.012

TOF Micromass, in positive mode. Absorption spectra were recorded using a Shimatzu UV-2450 spectrophotometer. Fluorescence experiments were performed using an Edinburgh Instruments FS920 and a HITACHI F4500 spectrofluorimeter, as indicated. The fluorescence lifetime was measured using an Edinburgh Instruments FL920 CD pumped by an EPL 404.2 nm laser, also from Edinburgh Instruments. The excitation and emission wavelengths ranged from 365 to 370 nm and 420–465 nm, respectively.

2.2. Photophysical characterization

2.2.1. Measurement of molar absorption coefficient

The molar absorption coefficient (ε) was determined from a single weighed sample dissolved in a stock solution that was subsequently diluted. The dilutions were made in such a way that the range of absorbance was from 0 to 1 (~10^{-5} to 10^{-6} mol/L) at the maximum wavelength and each measurement was made 5 times.

2.2.2. Fluorescence quantum yields (Φ_f)

The fluorescence quantum yields were measured by the relative standard method [15], in air saturated solutions, using perylene as a reference standard ($\Phi_f = 0.73$ in cyclohexane [16]) and a FS920 Edinburgh Instruments spectrofluorimeter with a Xenon Arc Lamp (Xe900, 450 W) and a TMS300 monochromator. In this method, the Φ_f of the sample were calculated from equation (1).

$$\Phi_{f\,X} = \Phi_{f\,ST} \times (G_X/G_{ST})\,(\eta_X^2/\eta_{ST}^2) \qquad 1$$

The subscripts ST and X denote standard and sample, respectively; Φ_f is the fluorescence quantum yield, G the slope from the plot of integrated area of the fluorescence intensity versus absorbance and η the refractive index of the solvent (for an example see SI Fig. 65). The sample and the reference were excited at the same wavelength, the same range of emission wavelengths was analyzed and both samples were maintained under the same experimental conditions.

For each Φ_f determination, the fluorescence spectra of isoabsorptive solutions (five samples in the absorbance range of 0.01–0.1 at the same wavelength) of the sample in an appropriate solvent (acetonitrile, dichloromethane, methanol and cyclohexane) relative to a standard solution of perylene in cyclohexane, were recorded using a 10 mm quartz cuvette.

2.2.3. Fluorescence lifetime (τ) measurements

Solutions with an absorbance of 0.1–0.5 at the absorption wavelengh (404.2 nm) were placed in quartz cuvettes. Fluorescence decay profiles of air saturated and argon-deoxygenated (15 min) solutions were recorded with the use of a fluorescence lifetime spectrometer FL920 from Edinburgh Instruments. Decays were monitored at the corresponding emission maxima of the compounds. The FAST software, Edinburgh Instruments, allowed the fitting of the decay spectra and yielded the fluorescence lifetimes.

2.3. Theoretical calculations

The theoretical calculations were performed using Gaussian 09 rev. C.01 [17]. The density functional methods B3LYP [18], PBE0 [19], CAM-B3LYP [20], ωB97X-D [21] were used in conjunction with Pople's double-ζ basis set augmented with diffuse functions and polarized with d orbitals [22]. Previous studies substantiate the effectiveness of this basis set for calculation of UV–vis spectra [23].

*2.4. Synthesis and characterization of **5***

The methyl benzo[*b*]carbazolediol ethers **5** were prepared as shown in Scheme 1. The substituents are detailed in Table 1. The first step was an oxidative coupling of naphthoquinone with anilines to give anilinonaphthoquinones (**3**), using catalytic quantities of copper acetate with acetic acid as the solvent [24]. The benzo[*b*]carbazolediones **4** were prepared by oxidative cyclization of **3** in an analogous fashion to a literature procedure [25]. The final step involved the one pot reduction and methylation using sodium dithionite and methyl iodide adapting a previously reported procedure [26].

*2.4.1. Preparation of compounds **4***

2-Anilino-1,4-naphthoquinone **3** (0,5 mmol), $Pd(OAc)_2$ (10 mol %), $Cu(OAc)_2.H_2O$ (20 mol%), K_2CO_3 (20 mol%) and pivalic acid (2 g) were added to a round bottomed flask and closed with a septum to which an oxygen filled balloon was connected. The reaction mixture was heated at 130 °C under an O_2 atmosphere for 14–20 h. The substrate consumption was monitored by TLC and after complete consumption the volatiles were removed under reduced pressure. The resulting crude product was taken up in a minimal volume of CH_2Cl_2 and applied to a column of chromatography silica gel. The column was eluted with CH_2Cl_2 and an EtOAc gradient. The fractions containing the product **4** were combined and the volatiles removed under reduced pressure.

*2.4.2. Preparation of compounds **5***

To the reaction flask were added: benzo[*b*]carbazolequinone **4** (0.25 mmol), $Na_2S_2O_4$ (2 mmol), Bu_4NBr (0.1–1 mmol) and a mixture of THF/H_2O (1:1V/V, 10 mL). The reaction flask was closed with a septum but allowed to pressure equalize with the atmosphere via an open syringe needle. The reaction was stirred at room temperature for about 1 h or until the reaction color had faded. Subsequently, NaOH (10 mmol) and an excess of CH_3I (1–2 mL) were added and the reaction was left stirring at room temperature for another hour. The crude product was isolated by partitioning the reaction between dichloromethane and water. The organic extracts were dried over Na_2SO_4, filtered and evaporated onto silica. The silica adsorbed product was applied to a short column of chromatography silica gel and the column eluted with dichloromethane. Fractions containing the product were identified by TLC, combined, and evaporated to give the isolated purified product.

*2.5. Spectroscopic structural characterization of compounds **5***

*2.5.1. 6,11-Dimethoxy-5-methylbenzo[b]carbazole **5a***

81% yield; FT-IR (cm^{-1}; KBr): 3062, 3030, 2987, 2931, 2850, 2831, 1633, 1604, 1462, 1444, 1394, 1363, 1296, 1083, 997, 765, 744; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.38 (3H, m); 7.48 (5H, m); 4.21 (6H, s); 4.09 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 147.2; 143.6; 134.9; 132.1; 127.2; 126.9; 125.0; 123.4; 122.4; 122.3; 122.0; 121.4; 120.7; 119.3; 118.0; 107.7; 62.9; 61.2; 31.1; ESI:HRMS (m/z+H$^+$): calculated 292.1332; found 292.1329 ($C_{19}H_{18}NO_2^+$).

*2.5.2. 6,11-Dimethoxy-3,5-dimethylbenzo[b]carbazole **5b***

57% yield. FT-IR (cm^{-1}, KBr). 3074, 3062, 3000, 2929, 2850, 2831, 1633, 1604, 1461, 1442, 1429, 1396, 1359, 1311, 1295, 1211, 1193, 1176, 1149, 1128, 1103, 1081, 1051, 1020, 995, 968, 950, 906, 838, 808, 769, 736, 707. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (1H, d, $J = 9.0$); 8.27 (2H, m); 7.56 (1H, t, $J = 6.0$); 7.47 (1H, t, 6.0); 7.20 (1H, s); 7.15 (1H, d, $J = 9.0$); 4.19 (6H, s); 4.08 (3H, s); 2.64 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.6; 143.9; 137.2; 134.7; 132.1; 126.8; 124.6; 124.3; 122.9; 122.2; 121.8; 120.6; 120.5; 118.8; 117.9; 108.0; 77.2; 62.8; 61.0; 30.8; 22.0; ESI:HRMS (m/z^+): calculated 305.1410; found 305.1414 ($C_{20}H_{19}NO_2^+$).