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The synthesis, characterization and optical properties of novel 1,3,4-oxadiazole-containing imidazo[1,5-*a*]pyridine derivatives

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ABSTRACT

A series of novel substituted 1,3,4-oxadiazole derivatives were synthesized by the reaction of 3-butyl-1-chloroimidazo[1,5-*a*]pyridine-7-carbohydrazide with propionyl chloride and substituted benzoic chloride in the presence of phosphorus oxychloride. The compounds were characterized using IR, ^{1}H NMR, ^{13}C NMR and HRMS. Absorption and fluorescence spectra were measured in dichloromethane; an intense absorption maxima was noted at ca. 290 nm and emission maxima was noted at ca. 470 nm. The absorption spectra of the 1,3,4-oxadiazole derivatives reveal that a phenyl and an ethyl group attached to the 1,3,4-oxadiazole ring markedly influenced the maximum absorption. The structures based on density function theory (DFT) calculation show planar configurations for the compounds. The calculated molecular orbital correlates well with their absorption.

1. Introduction

Imidazo[1,5-*a*]pyridines have attracted increasing attention due to their pharmaceutical applications such as cardiotonic agents [1], aromatase inhibitors in estrogen-dependent diseases [2], thromboxane A2 synthetase inhibitors [3], and angiotensin II receptor antagonists [4]. They also have potential applications in organic light-emitting diodes (OLEDs) [5–7], in organic thin-layer field effect transistors (FETs) [8], and as precursors of N-heterocyclic carbenes [9].

1,3,4-Oxadiazole derivatives have attracted significant interest in electro-active and opto-active materials, since these compounds possess high electron-accepting properties and exhibit strong fluorescence with high quantum yields [10]. The quantum yields of 2,5-diphenyl-1,3,4-oxadiazole and 2,5-di-2-naphthyl-1,3,4-oxadiazole were reported to be 0.80 and 0.85 in cyclohexane solutions, respectively [11]. Thus, compounds involving 1,3,4-oxadiazole rings have been used as electron-transporting materials and emitters in organic EL devices [12–14]. Small molecular oxadiazole derivatives, such as 2-(4-tert-butylphenyl)-5-biphenyl-1,3,4-oxadiazole (PBD), have also been commonly used as electron-transporting and hole-blocking materials in OLEDs [15–20]. Although a number of papers have been published concerning the synthesis of 1,3,4-oxadiazole fluorescent compounds, those containing a new heterocyclic system of imidazo[1,5-*a*]pyridine moiety have not yet been reported. Thus, combining 3-butyl-1-chloroimidazo[1,5-*a*]pyridine moiety with substituted 1,3,4-oxadiazole is expected to give new fluorescent compounds.

This work describes the synthesis, characterization and optical properties of novel, substituted 1,3,4-oxadiazole-containing imidazo[1,5-*a*]pyridine derivatives.

2. Experimental

2.1. General

Thin-layer chromatography (TLC) was conducted on silica gel 60 F_{254} plates (Merck KGaA). ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer, using DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Melting points were determined on a XD-4 digital micromelting point apparatus. IR spectra were recorded with an IR spectrophotometer VERTEX 70 FT-IR (Bruker Optics). HRMS spectra were recorded on a Q-TOF6510 spectrograph (Agilent). UV–vis spectra were recorded on a U-4100 (Hitachi). Fluorescent measurements were recorded on a PerkineElmer LS-55 luminescence spectrophotometer.

2.2. Computation details

The hybrid density function B3LYP (Becke–Lee–Young–Parr composite of exchange-correction functional) method [21,22] and the standard 6–31 G (d, p) basis set [23] were used for both structure optimization and the property calculations. All the calculations were performed using the Gaussian 03 program in

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the IBM P690 system at the Shandong Province High Performance Computing Center.

2.3. Synthesis

The synthetic routes of the proposed compounds **8** are outlined in Fig. 1.

2.3.1. Preparation of 2-butyl-4-chloro-1H-imidazole-5-carbaldehyde (4)

Compound **4** was synthesized according to the literature method [24]. Reaction of compound **3** with $POCl_3$/DMF was followed by hydrolysis, giving 2-butyl-5-chloro-3*H*-imidazole-4-carbaldehyde **4** with the yield of 68%.

2.3.2. Preparation of ethyl 3-butyl-1-chloroimidazo[1,5-a] pyridine-7-carboxylate (5)

To a 50-mL round-bottomed flask were added **4** (1.00 mmol), an ethyl 4-bromobut-2-enoate (2.00 mmol), potassium carbonate (0.28 g, 2.05 mmol) and dry DMF (10 mL). The mixture was stirred at r.t for 3 h and then filtered. The filtrate was poured into water (100 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined extracts were washed with water, dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The crude products were purified by column chromatography to afford compound **5** with the yield of 86%.

Yellow solid: mp 56–58 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.23 (dd, J=7.2, 0.8 Hz, 1H), 7.95 (d, J=1.2 Hz, 1H), 6.99 (dd, J=7.2, 1.6 Hz, 1H), 4.30 (q, J=7.2 Hz, 2H), 2.96 (t, J=7.6 Hz, 2H), 1.69 (m, 2H), 1.35 (m, 5H), 0.89 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.9, 139.4, 123.3, 121.8, 121.2, 119.7, 119.2, 110.6, 60.8, 28.3, 25.1, 21.7, 13.9, 13.5; IR (KBr) ν=2932, 2879, 1714, 1124, 1100, 751 cm^{-1}; HRMS: *m/z* calcd for $C_{14}H_{18}ClN_2O_2$ $[M+H]^+$ 281.1057, found 281.1062.

2.3.3. Preparation of 3-butyl-1-chloroimidazo[1,5-a] pyridine-7-carbohydrazide (6)

To a stirred solution of compound **5** (1 mmol) in ethanol (5 mL), 80% hydrazine monohydrate (1.2 mL) was added. The reaction mixture was maintained under reflux for 6 h. After this time, the reaction mixture was cooled to room temperature and left overnight, and white solid was precipitated. The crude product was collected by filtration and then recrystallized from ethanol to afford compound **6** with the yield of 88%.

Yellow solid: mp 167–168 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.89 (s, 1H), 8.23 (d, J=7.2 Hz, 1H), 7.95 (s, 1H), 7.08 (dd, J=7.2, 1.6 Hz, 1H), 4.53 (s, 2H), 2.96 (t, J=7.6 Hz, 2H), 1.69 (m, 2H), 1.35 (m, 2H), 0.89 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.8, 138.6, 123.6, 123.3, 121.8, 119.2, 115.9, 110.5, 28.5, 25.1, 21.7, 13.6; IR (KBr) ν=3321, 2958, 2870, 1648, 1511, 1256, 1107, 739 cm^{-1}; HRMS: *m/z* calcd for $C_{12}H_{16}ClN_4O$ $[M+H]^+$ 267.1013, found 267.1009.

2.3.4. General procedure for the preparation of 8a–g

A solution of propionyl chloride or substituted benzoyl chloride (2 mmol) in $CHCl_3$ (5 mL) was added dropwise to a solution of compound **6** (0.60 g, 2 mmol), triethylamine (0.30 mL, 2 mmol) and $CHCl_3$ (10 mL) at r.t. The resulting mixture was stirred for 12 h. The solvent was removed and the crude product **7** was washed with petroleum ether and water. The solid was dried and added to phosphorus oxychloride (10 mL, Caution: reacts violently with water; incompatible with many metals, alcohols, amines, phenol, DMSO, and strong bases). The mixture was refluxed for 12 h. Excess $POCl_3$ was distilled off and the residue was poured into iced water. The precipitate was filtered, washed with water, dried and recrystallized from ethanol to give compound **8** with the yield of 62–86%.

*2.3.4.1. 2-(3-Butyl-1-chloroimidazo[1,5-a]pyridin-7-yl)-5-ethyl-1,3,4-oxadiazole (**8a**).* Yellow solid (62% yield): mp 124–125 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.36 (dd, J=7.6, 0.4 Hz, 1H), 7.91 (s, 1H), 7.15 (dd, J=7.6, 1.6 Hz, 1H), 2.96 (m, 4H), 1.71(m, 2H), 1.33 (m, 5H), 0.89 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.0, 163.2, 139.4, 124.2, 121.9, 121.1, 116.7, 114.1, 110.6, 29.0, 26.2, 22.4, 19.0, 13.7, 10.8; IR (KBr) ν=2956, 2869, 1711, 1638, 1561, 1491, 1288, 1067, 791 cm^{-1}; HRMS: *m/z* calcd for $C_{15}H_{18}ClN_4O$ $[M+H]^+$ 305.1169, found 305.1175.

*2.3.4.2. 2-(3-Butyl-1-chloroimidazo[1,5-a]pyridin-7-yl)-5-phenyl-1,3,4-oxadiazole (**8b**).* Yellow solid (71% yield): mp 164–165 °C;

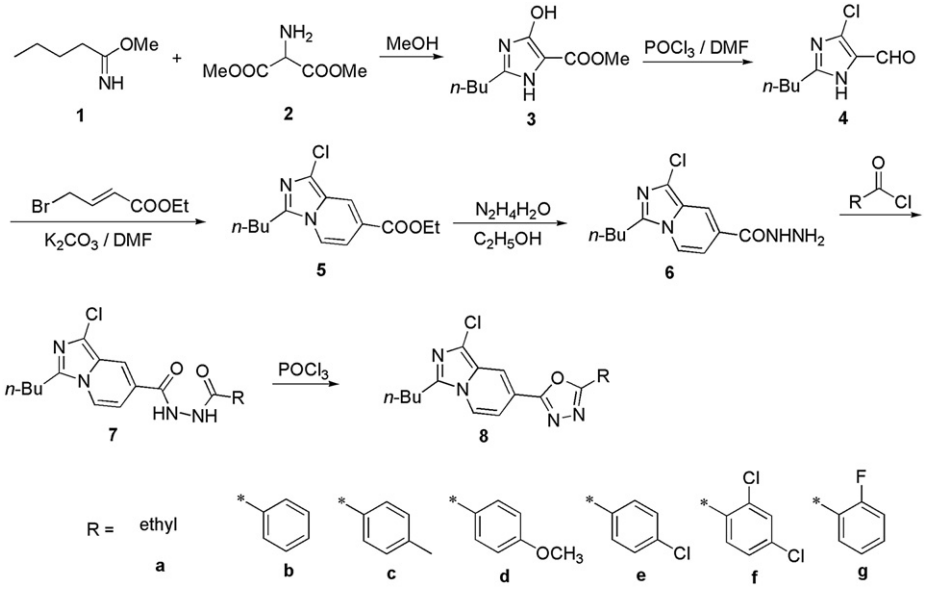

Fig. 1. Synthesis of substituted 1,3,4-oxadiazole derivatives.