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Short Note

New 2-(2,4-Dihydroxyphenyl)benzimidazolines

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Abstract: New 2-(2,4-dihydroxyphenyl)benzimidazolines are synthesized in an easily accessible approach. The method is based on the reaction of resorcinol with in situ-formed electrophilic *N*-ethoxycarbonylbenzimidazolium reagents. The structure of the two newly formed products was spectrally characterized by 1D and 2D NMR, IR, and MS spectral analyses.

Keywords: benzimidazole; resorcinol; benzazoles; *N*-acylbenzimidazolium ions; in situ reactions

1. Introduction

Derivatives of 2-substituted benzimidazole play a useful structural motif for the development of molecules with pharmaceutical interests [1–3]. The benzimidazole skeleton containing an aryl substituent at C-2 is part of an important class of bicyclic privileged substructures with powerful effectiveness as enzyme inhibitors [4,5], antimicrobials [6], antiprotozoal agents [7], antioxidants [8], with cytotoxic activity [9–11], luminescent [12] and fluorescent materials [13,14], etc.

On the other hand, phenolic compounds are of exceptional interest for organic synthesis, including their application for the development of new medicinals [15]. Many of them have proven antioxidant activity and application for the treatment of various cardiovascular, neurological, and cancer diseases [16]. Some phenols (such as resorcinol) occur in low concentrations as free phenolic substances in plants [17]. In addition, the possibility of the application of resorcinol in antimicrobial textiles was recently reported [18], as well as the immunomodulatory potential of new benzothiazole–resorcinol hybrids [19].

In this regard, a series of condensation reactions of 1,2-phenylenediamine and aldehyde using the following catalysts: cobalt(II) hydroxide [20], sodium dithionite [21], sodium disulfite [22], sodium hydrogen sulfite in ethanol [23], and sodium metabisulfite [24] have been recently published for the synthesis of 2-(2,4-dihydroxyphenyl)benzimidazoles. Nevertheless, synthetic data for the modification of benzimidazole ring with resorcinol by an α-amidoalkylation reaction were still not found in the literature.

Reactions of α-amidoalkylation play an important role in organic synthesis for the building of carbon–carbon or carbon–heteroatom bonds. This method has some advantages over the known Mannich reaction. A wide range of nitrogen containing amidoalkylation precursors are used to generate *N*-acylimines or *N*-acyliminium ions as highly reactive intermediates [25]. *N*-acyliazolinium salts prepared in situ have been used in reactions with 2-silylazoles [26], allyltributyltin compounds [27], silyl enol ethers [28], and organoindium reagents [29]. The current direction of our scientific group is developing an accessible approach for the amidoalkylation of various heterocycles. In this context, we recently reported 1-pot synthesis of various 2-hydroxyphenyl-benzothiazolines as potential antimicrobials active against *Bacillus licheniformis* MIC = 0.0008–0.0500 mg/mL and *Staphylococcus aureus* MIC = 0.0016–0.0125 mg/mL, as well as new quercetin hybrids with radical scavenging profile with varied IC_{50} values in the range of 6.17 ± 0.3–7.26 ± 0.3 μM measured with DPPH assay, and 49.8 ± 3.5–62.4 ± 3.5 μM with ABTS assay [30,31].

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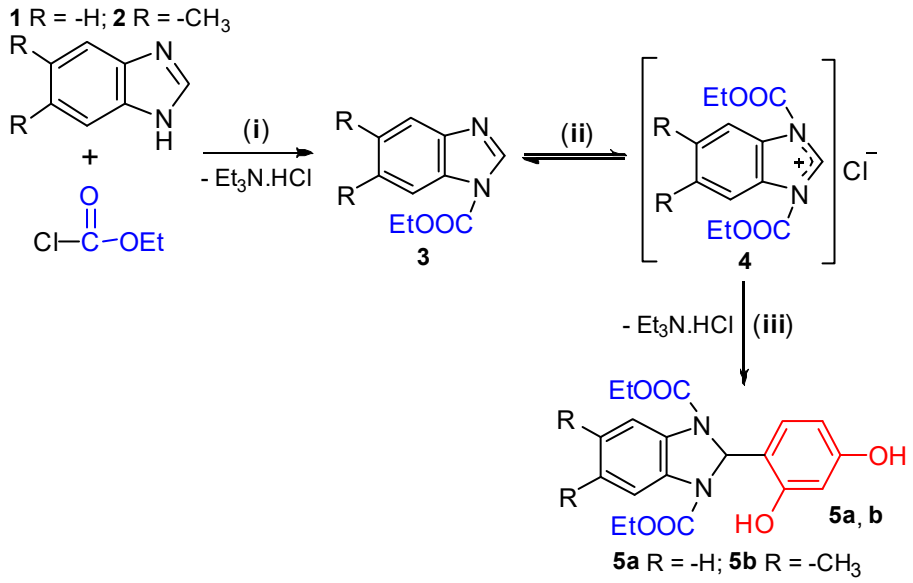
The aim of this study is to apply the same manner for the modification of the benzimidazole ring with resorcinol.

2. Results and Discussion

Motivated by the previous successful work for the synthesis of quercetin-containing benzimidazole hybrids [31], here, we report our current investigations on the application of adducts (**4**) obtained from benzimidazole and 5,6-dimethylbenzimidazole (**1**,**2**) with ethyl chloroformate for the amidoalkylation of resorcinol. The above-mentioned reactions lead to products (**5a**,**b**) according to Scheme 1.



Scheme 1. Synthesis of *N*,*N*-diethoxycarbonyl-2-(2,4-dihydroxyphenyl)benzimidazolines (**5a**,**b**) by reaction of α-amidoalkylation; (**i**) CH_2Cl_2, Et_3N, 0 °C, 20 min.; (**ii**) ClCOOEt, r.t., 60 min.; and (**iii**) Resorcinol dissolved in CH_3CN, Et_3N, r.t., 5 h.

The reaction conditions, including the ratio of the reagents and time, are presented in Table 1.

Table 1. The ratio of the reagents, reaction time and yields of **5a** and **5b**, Scheme 1 (iii).

Product 5	R	Ratio *	Time, h	Yield, %
a	H	1:1	24	50
a	H	1:2	5	89
b	Me	1:1	24	56
b	Me	1:2	5	92

* ratio of *N*,*N*-diethoxycarbonylbenzimidazolium ions: resorcinol.

The reactions were successfully completed under room temperature (20–25 °C) for 5 h. It was found that dichloromethane is a suitable solvent for carrying out the reactions. The best yields of products (89%, **5a**) and (92%, **5b**, Table 1) were obtained with the continuous addition of 2 equivalents of resorcinol dissolved in 3 milliliters of acetonitrile. In the course of the reactions, triethylamine was added as a hydrochloric scavenger. Table 1 indicates the reaction conditions under which the monosubstituted products were obtained with the highest yields. It is found that the yield scope depended on the stability of the products in an acidic medium. The unexpected mixture of compounds (monitored by TLC) was observed using an equimolar ratio of starting reagents according to our previously published study [30]. For the reactions of *N*-acylation with benzimidazole and

5,6-dimethylbenzimidazole, the presence of Et_3N as a hydrochloric scavenger was required and established at 0 °C.

The products are successfully crystallized using a mixture of petroleum/diethyl ether. Relatively pure samples of monosubstituted benzimidazolines were isolated by column chromatography on silica gel.

The structure of products (**5a**,**b**) was confirmed by 1D and 2D NMR, IR, and MS spectral data. To average out the rotamers observed in *N*,*N*-diethoxycarbonyl-benzimidazolines reaching adequate assignment of peaks and structure determination, the NMR spectra were measured at 80 °C in DMSO-d_6. The ^{1}H-NMR spectra of the analyzed compounds indicate an easily recognizable set of quartets about δ = 4.10 ppm and triplets about δ = 1.15 ppm for the protons from 2 methyl- and methylene- groups part of diethoxycarbonyl fragments. Furthermore, singlets for the proton on sp^3- C-2 atom in benzimidazole rings were observed in the range of δ = 6.90–6.93 ppm. The ^{1}H-, ^{13}C-HSQC measurements proved the exact location of these characteristic signals, including the position of substitution. Consequently, the protons from OH groups are detected as a brought singlet at 9.93 ppm for **5a** and 9.04 ppm for **5b**. The signals of ^{13}C-NMR spectra comply with all carbon atoms from the expected structures. Analyzing the IR spectra also gives us enough evidence for the presence of the expected structural fragments and functional groups (see fully associated IR bands in the Materials and Methods section).

The original 1D and 2D NMR, IR, and MS spectra of the molecules are available in the Supplementary Materials Section (S1).

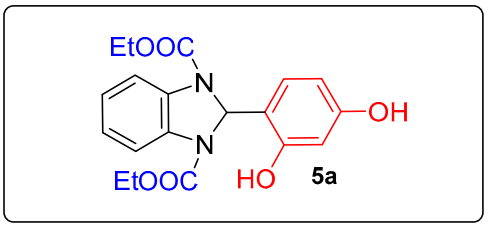
3. Materials and Methods

Benzimidazole [CAS No. 51-17-2], 5,6-dimethylbenzimidazole [CAS No. 582-60-5], triethylamine [CAS No. 121-44-8], ethyl chloroformate [CAS No. 541-41-3], resorcinol [CAS No. 108-46-3], and the dry organic solvents were purchased from Sigma-Aldrich, Merck (Darmstadt, Germany).

Melting points were measured on a Kruss M5000 melting point meter (A.Krüss Optronic GmbH, Hamburg, Germany). IR spectra were measured on an ALPHA II FT-IR spectrometer (Bruker Optics GmbH, Ettlingen, Germany). High-resolution mass spectral measurements were performed on a Bruker mass spectrometer. ^{1}H-, ^{13}C-NMR spectra were measured on Bruker Avance NEO AV400 spectrometer (Bruker, Billerica, MA, USA) at BAS-IOCCP—Sofia, and chemical shifts (δ, ppm) are downfield from TMS. TLC was done on precoated 0.2 mm Merck silica gel 60 plates. Silica gel was used for column chromatography.

*Synthesis of 2-(2,4-Dihydroxyphenyl)benzimidazolines (***5a**,**b***), General Procedure*

The ethyl chloroformate (1.2 mmol, 0.12 mL) was added dropwise to a magnetically stirred solution of benzimidazole (1 mmol, 0.118 g) or 5,6-dimethylbenzimidazole (1 mmol, 0.146 g) and triethylamine (1 mmol, 0.14 mL) in 10 mL dichloromethane at 0 °C. After 20 min, another 1.2 mmol ethyl chloroformate was added, and the reaction mixture was transferred at room temperature (20–25 °C) for 60 min. Then, resorcinol (0.220 g, 2 mmol) dissolved in 3 mL acetonitrile was added dropwise to the reaction mixture for the course of 30 min. Thereafter, triethylamine (1 mmol, 0.14 mL) dissolved in dichloromethane (5 mL) was sequentially added dropwise to the reaction mixture for a period of 60 min as a hydrochloric scavenger. Then, the reaction was continued under the conditions described in Table 1. After completion of the reaction (monitored by TLC), the reaction mixture was dissolved in chloroform (30 mL) and washed successively with 1% HCl (40 mL) and water (40 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The products were isolated by crystallization with mixtures of petroleum/diethyl ether. Relatively pure samples (TLC) are obtained with filtration through short-column chromatography on silica gel.



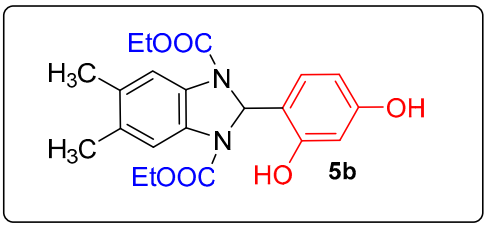
Compound **5a** (Diethyl 2-(2,4-dihydroxyphenyl)-1*H*-benzo[*d*]imidazole-1,3(2*H*)-dicarboxylate) was a white powder isolated by crystallization with a mixture of petroleum/diethyl ether 4:1, Rf = 0.3 (petroleum:diethyl ether 1:2). Its yield: (0.33 g, 89%), m.p.: 204–206 °C, accompanied by decomposition and darkening;

^{1}H-NMR (400 MHz, 80 °C, DMSO-d$_6$, δ ppm, *J* Hz): 9.07 (s, 2H, 2x-OH), 7.59 (dd, *J* = 5.9, 3.3 Hz, 2H, 2x-CH-benzimidazole), 6.99 (dd, *J* = 5.9, 3.4 Hz, 2H, 2x-CH-benzimidazole), 6.93 (s, 1H, -*CH), 6.89 (d, *J* = 8.4 Hz, 1H, -CH-resorcinol), 6.23 (d, *J* = 2.4 Hz, 1H, -CH-resorcinol), 6.17 (dd, *J* = 8.4, 2.5 Hz, 1H, -CH-resorcinol), 4.10 (q, *J* = 7.0 Hz, 4H, 2x-COCH$_2$CH$_3$), 1.15 (t, *J* = 7.0 Hz, 6H, 2x-COCH$_2$CH$_3$);

^{13}C-NMR (101 MHz, 80 °C, DMSO-d$_6$, δ ppm, *J* Hz): 159.2(-C-OH), 156.9 (-C-OH), 151.3 (2x-COCH$_2$CH$_3$), 133.2 (-2xC-benzimidazole), 129.8 (-CH), 123.0 (-CH), 116.9 (-CH), 113.6 (-CH), 106.7 (-CH), 103.2 (-CH), 74.5 (-*CH), 61.8 (2x-COCH$_2$CH$_3$), 14.4 (2x-COCH$_2$CH$_3$);

HRMS *m/z* (ESI): calcd for $C_{19}H_{19}N_2O_6^-$ [M-H]$^-$ 371.1249, found 371.1250;

IR (KBr, cm^{-1}): 3380 (O-H), 2982, 2931, 2906 (Csp^3-H), 1695 (C=O), 1594, 1504, 1416 (C=C), 1383 (O-H), 1317 (C-N), 1285 (C-O-C), 1203 (C-O), 1184 (C-CO-C), 1096, 1049, 1020 (C-N).



Compound **5b** (Diethyl 2-(2,4-dihydroxyphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1,3(2*H*)-dicarboxylate) was a white powder isolated by crystallization with a mixture of petroleum/diethyl ether 8:1, Rf = 0.75 (diethyl ether). Its yield: (0.37 g, 92%), m.p.: 217–219 °C, accompanied by decomposition and darkening;

^{1}H-NMR (400 MHz, 80 °C, DMSO-d$_6$, δ ppm, *J* Hz): 9.04 (s, 2H, 2x-OH), 7.39 (s, 2H, 2x-CH-5,6-dimethylbenzimidazole), 6.90 (s, 1H, -*CH), 6.85 (d, *J* = 8.4 Hz, 1H, -CH-resorcinol), 6.22 (d, *J* = 2.3 Hz, 1H, -CH-resorcinol), 6.15 (dd, *J* = 8.4, 2.4 Hz, 1H, -CH-resorcinol), 4.08 (q, *J* = 7.1 Hz, 4H, 2x-COCH$_2$CH$_3$), 2.21 (s, 6H, 2x-CH$_3$), 1.14 (t, *J* = 7.1 Hz, 6H, 2x-COCH$_2$CH$_3$);

^{13}C-NMR (101 MHz, 80 °C, DMSO-d$_6$, δ ppm, *J* Hz): 159.1 (-C-OH), 156.8 (-C-OH), 151.2 (2x-COCH$_2$CH$_3$), 131.1 (-2C-5,6-dimethylbenzimidazole), 130.3 (-2C-5,6-dimethylbenzimidazole), 129.4 (-CH), 117.1 (-CH), 115.0 (-CH), 106.7 (-CH), 103.2 (-CH), 74.2 (-*CH), 61.7 (2x-COCH$_2$CH$_3$), 19.8 (2x-CH$_3$), 14.4 (2x-COCH$_2$CH$_3$);

HRMS *m/z* (ESI): calcd for $C_{21}H_{23}N_2O_6^-$ [M-H]$^-$ 399.1562, found 399.1564;

IR (KBr, cm^{-1}): 3345 (O-H), 2980, 2935, 2865 (Csp^3-H), 1697 (C=O), 1611, 1516, 1461 (C=C), 1383 (O-H), 1320 (C-N), 1297 (C-O-C), 1260 (C-O), 1162 (C-CO-C), 1100, 1076, 1026 (C-N).

4. Conclusions

We have successfully synthesized two new 2-(2,4-dihydroxyphenyl) benzimidazolines, employing an efficient high-yielding approach. The applied *N*-acylliminium reagents formed in situ from benzimidazole or 5,6-dimethylbenzimidazole and ethyl chlorformate react with resorcinol, providing access to *N*,*N*-diethoxycarbonyl-benzimidazolines contain-

ing resorcinol fragment in the moiety. The obtained products are interesting because of their potential biological activities.

Supplementary Materials: The following supporting information can be downloaded online. S1.pdf—processed ^{1}H-, ^{13}C-NMR, HSQC, IR and MS spectra. 2-(2,4-dihydroxyphenyl)benzimidazolines **5a**,**b** mol files.

Author Contributions: Manuscript writing: Y.S.; revising and final English check: S.S.-A.; chemical synthesis: D.K., M.B. and Y.S.; spectral analysis: Y.S. and M.B. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available in this article and supporting information.

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Conflicts of Interest: The authors declare no conflict of interest.

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