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LETTERS TO THE EDITOR

Spectral Luminescent Properties of 2-Aryl-5-(2,6-dimethoxyphenyl)-1*H*-1,3,4-oxadiazoles

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Abstract—2-Aryl-5-(2,6-dimethoxyphenyl)-1*H*-1,3,4-oxadiazoles were synthesized by cyclization reaction of benzoylbenzohydrazides in $SOCl_2$, and their spectral luminescent properties were studied. The oxadiazoles containing phenyl or *o*-methoxyphenyl substituents in the position 2 were shown to luminesce with a high quantum yield in polar and nonpolar solvents. The replacement of these substituents by 2-hydroxyphenyl group led to oxadiazole intensely emitting only in highly polar aprotic DMSO.

Keywords: 2,5-diaryl-1,3,4-oxadiazoles, luminescence, luminescence quantum yield, organic phosphors
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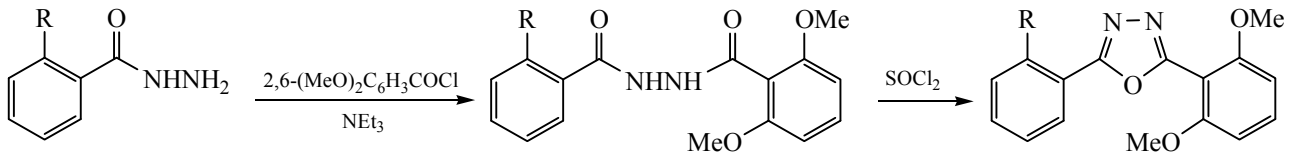
1,3,4-Oxadiazoles and their derivatives belong to one of the most intensively studied classes of five-membered nitrogen-containing heterocycles characterized by good synthetic accessibility and high structural variability, as well as by wide range of practical applicability. These compounds have diverse biological activity [1] and are extensively used in various fields of medicinal chemistry [2] and pesticide chemistry [3]. Also, they possess interesting spectral luminescent properties making them suitable for the preparation of widely demanded organic [4–7] and metal complex-based [8, 9] phosphors.

For expanding the range of compounds of this class and for studying their spectral luminescent properties we applied here the reaction of hydrazides **1a–1c** with 2,6-dimethoxybenzoic acid chloride in the presence of triethylamine to obtain benzoylbenzohydrazides **2a–2c** whose subsequent cyclization with thionyl chloride led to 2-aryl-5-(2,6-dimethoxyphenyl)-1*H*-1,3,4-oxadiazoles **3a–3c** (Scheme 1).

In the absorption spectra of oxadiazoles **3a–3c** the maximum of the long-wave band due to π→π* electron transitions is observed within the 256–316 nm range, consistent with their benzenoid structure. The luminescence spectra of oxadiazole **3b** in isooctane, toluene, and acetonitrile contain two bands: a short-wave band (λ^{fl}_{max} 353–378 nm, φ 0.001–0.012) which has a normal Stokes shift (3019–4992 cm^{-1}) and a long-wave band (λ^{fl}_{max} 479–482 nm, φ 0.006– 0.013) which has an anomalously large Stokes shift (10471–

Scheme 1.



1a–1c **2a–2c** **3a–3c**

R = H (**a**), OH (**b**), OMe (**c**).

10799 cm^{-1}). Based on the fluorescence excitation spectra the short-wave band was assigned to the initial benzenoid structure **3**, and the long-wave luminescence was associated with the emission of a short-lived phototautomer resulting from an excited-state intramolecular proton transfer (ESIPT) from the phenolic hydroxy group to the closest nitrogen atom of the heterocycle [10, 11]]. A low total luminescence quantum yield exhibited for oxadiazole **3b** (φ 0.013–0.019) is due to nonradiative deactivation of its excited state by the ESIPT mechanism. However, in highly polar DMSO the spectrum of oxadiazole **3b** contains only one short-wave high-intensity band (λ^{fl}_{max} 363 nm, φ 0.15) with a normal Stokes shift (4098 cm^{-1}) assigned to the initial benzenoid structure **3b** basing on the fluorescence excitation spectra. This is explained by strong intermolecular hydrogen bonding between the phenolic hydroxy group of oxadiazole **3b** and highly polar aprotic DMSO inhibiting the ESIPT process. Oxadiazoles **3a** and **3c** where an ESIPT process is impossible because of the absence of a mobile proton of the phenolic OH group emit intensely in a closely adjacent spectral region (λ^{fl}_{max} 352–363 nm, φ 0.11–0.33). Similar spectral behavior was previously observed in 1,3,4-oxadiazoles structurally similar to compounds **3a–3c** [11–15].

Thus, the replacement of the *ortho*-phenolic substituent in 2-(2-hydroxyphenyl)-5-(2,6-dimethoxyphenyl)-1*H*-1,3,4-oxadiazole **3b** by phenyl or *ortho*-methoxyphenyl group blocks the ESIPT process in oxadiazoles **3a** and **3c** formed, leading to strong enhancement of the luminescence quantum yield in nonpolar solvents and in acetonitrile compared to oxadiazole **3b**. This allows these compounds to be included among widely demanded oxadiazole series organic phosphors emitting in the short-wave region of the visible spectrum.

***N*'-Benzoyl-2,6-dimethoxybenzohydrazide (2a).** To a solution of 1.36 g (0.01 mol) of benzoic acid hydrazide **1a** in 20 mL of anhydrous acetonitrile, 5 mL of triethylamine and 2.01 g (0.01 mol) of 2,6-dimethoxybenzoic acid chloride in 30 mL of anhydrous acetonitrile were added successively with stirring. The reaction mixture was left for 1 day at room temperature and then refluxed for 3 h. The solvent was distilled off in a vacuum to give an oily residue which was washed with water (2 × 10 mL) and air-dried, whereupon the resulting product was isolated by column chromatography (eluent ethyl acetate–petroleum ether, 1 : 2), with the R_f 0.75–0.78 fraction being collected. After the solvent was distilled off, the product was recrystallized from 2-propanol (2 × 15 mL). Yield 2.46 g (82%), colorless crystals, mp 196–198°C. IR spectrum, ν, cm^{-1}: 765, 821, 1010, 1124, 1170, 1237, 1260, 1278, 1478, 1499, 1542; 1573, 1597, 1621 (C=C); 1655, 1698 (C=O); 3180 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.83 s (6H, 2,6-OCH_3), 6.57 d (2H, H_{Ar}, J = 8.4 Hz), 7.24 t (1H, H_{Ar}, J = 8.4 Hz), 7.41–7.55 m (3H, H_{Ar}), 7.84 d.d (2H, H_{Ar}, J_1 = 1.2, J_2 = 7.5 Hz), 9.12 d (1H, NH, J = 3.8 Hz), 9.32 d (1H, NH, J = 3.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 56.32 (2OCH_3), 101.32 (C_{Ar}), 104.83 (2C_{Ar}), 127.92 (2C_{Ar}), 128.03 (C_{Ar}), 128.99 (2C_{Ar}), 132.32 (C_{Ar}), 133.05 (C_{Ar}), 158.13 (2C_{Ar}), 163.42 (C=O), 166.33 (C=O). Found, %: C 64.05; H 5.35; N 9.38. $C_{16}H_{16}N_2O_4$. Calculated, %: C 63.99; H 5.37; N 9.33.

***N*'-(2-Hydroxybenzoyl)-2,6-dimethoxybenzohydrazide (2b)** was prepared in a similar manner by the reaction of salicylic acid hydrazide **1b** with 2,6-dimethoxybenzoic acid chloride. Yield 2.31 g (73%), colorless crystals, mp 223–224°C (mp 222–225°C [16]). IR and ^{1}H and ^{13}C NMR spectra of **2b** corresponded to those presented in [16]**.**

***N*'-(2-Methoxybenzoyl)-2,6-dimethoxybenzohydrazide (2c)** was prepared in a similar manner by the reaction of *o*-methoxybenzoic acid hydrazide **1c** with 2,6-dimethoxybenzoic acid chloride. Yield 2.61 g (79%), colorless crystals, mp 150–152°C. IR spectrum, ν, cm^{-1}: 732, 757, 804, 1003, 1125, 1168, 1188, 1233, 1264, 1297, 1479; 1562, 1625 (C=C); 1670, 1701 (C=O); 3137 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.82 s (6H, 2,6-OCH_3), 4.06 s (3H, OCH_3), 6.55 d (2H, H_{Ar}, J = 8.4 Hz), 6.90–7.11 m (2H, H_{Ar}), 7.29 d.d (1H, H_{Ar}, J_1 = 7.5, J_2 = 7.6 Hz), 7.47 d.d (1H, H_{Ar}, J_1 = 7.6, J_2 = 8.2 Hz), 8.08 d.d (1H, H_{Ar}, J_1 = 1.2 , J_2 = 7.5 Hz), 9.65 d (1H, NH, J = 4.2 Hz), 11.17 d (1H, NH, J = 4.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 55.93 (2OCH_3), 56.01 (OCH_3), 102.17 (C_{Ar}), 105.15 (2C_{Ar}), 112.47 (C_{Ar}), 115.18 (C_{Ar}), 121.63 (C_{Ar}), 128.32 (C_{Ar}), 129.17 (C_{Ar}), 132.84 (C_{Ar}), 157.93 (C_{Ar}), 159.12 (2C_{Ar}), 161.33 (C=O), 165.74 (C=O). Found, %: C 61.88; H 5.47; N 8.53. $C_{17}H_{18}N_2O_5$. Calculated, %: C 61.81; H 5.49; N 8.48.

2-(2,6-Dimethoxyphenyl)-5-phenyl-1,3,4-oxadiazole (3a). A solution of 2.40 g (0.008 mol) of benzohydrazide **2a** in 50 mL of thionyl chloride was refluxed for 6 h. The solvent was distilled off in a vacuum, and the reaction mass was cooled to room temperature and poured over 50 g of crushed ice. The resulting precipitate was filtered off, and the crystalline product was purified by column chromatography

(eluent ethyl acetate-petroleum ether, 1: 2), with the R_f 0.75–0.80 fraction being collected. After the solvent was distilled off the product was recrystallized from 2-propanol. Yield 1.40 g (62%), colorless crystals, mp 164–166°C. IR spectrum, ν, cm^{-1}: 755, 787, 804, 963, 986, 1012, 1037, 1125, 1169, 1240, 1276, 1285, 1438, 1464, 1471; 1480; 1551, 1560, 1593 (C=C); 1610, 1632 (C=N). UV spectrum, λ_{max}, nm [$\varepsilon\times10^{-4}$ L mol^{-1} cm^{-1}, λ_{exc} 300 nm]: isooctane, 205 [2.92], 290 [0.95], λ^{fl}_{max} (φ) 358 (0.11); acetonitrile, 257 [1.36], 318 [0.83], λ^{fl}_{max} (φ) 359 (0.12); DMSO, 315 [1.18], λ^{fl}_{max} (φ) 357 (0.23). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.79 s (6H, 2,6-OCH_3), 6.62 d (2H, H_{Ar}, J = 8.4 Hz), 7.43 t (1H, H_{Ar}, J = 8.4 Hz), 7.45–7.52 m (3H, H_{Ar}), 8.03–8.17 m (2H, H_{Ar}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 56.10 ($2OCH_3$), 102.89 (C_{Ar}), 103.87 ($2C_{Ar}$), 124.46 (C_{Ar}), 127.00 ($2C_{Ar}$), 128.93 ($3C_{Ar}$), 131.40 (C_{Het}), 133.56 (C_{Het}), 159.96 ($2C_{Ar}$), 165.27 (C_{Ar}). Found, %: C 68.15; H 4.99; N 9.97. $C_{16}H_{14}N_2O_3$. Calculated, %: C 68.08; N 5.00; N 9.92.

2-[5-(2,6-Dimethoxyphenyl)-1,3,4-oxadiazol-2-yl]-phenol (3b) was prepared in a similar manner by the cyclization of benzohydrazide **2b** in thionyl chloride. Yield 1.17 g (49%), colorless crystals, mp 93–95°C. IR spectrum, ν, cm^{-1}: 758, 831, 974, 1003, 1035, 1056, 1141, 1158, 1240, 1272, 1285, 1300, 1402, 1453, 1471, 1490; 1544, 1559 (C=C); 1598, 1629 (C=N); 3201 (OH). UV spectrum, λ_{max}, nm [$\varepsilon\times10^{-4}$ L mol^{-1} cm^{-1}, λ_{exc} 300 nm]: isooctane, 257 [1.85], 263 [1.77], 307 [1.25], 318 [1.12], λ^{fl}_{max} (φ) 364 (0.001), 481 (0.012); toluene, 309 [1.18], 317 [1.08], λ^{fl}_{max} (φ) 378 (0.006), 482 (0.013); acetonitrile, 304 [0.74], 319 [0.62], λ^{fl}_{max} (φ) 353 (0.012), 479 (0.006); DMSO, 304 [0.74], 316 [0.62], λ^{fl}_{max} (φ) 363 (0.15). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.81 s (6H, 2,6-OCH_3), 6.65 d (2H, H_{Ar}, J = 8.4 Hz), 6.97 t (1H, H_{Ar}, J = 8.4 Hz), 7.11 d.d (1H, H_{Ar}, J_1 = 1.1, J_2 = 7.6 Hz), 7.36–7.48 m (2H, H_{Ar}), 7.78 d.d (1H, H_{Ar}, J_1 = 1.8, J_2 = 7.9 Hz), 10.31 (1H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 56.14 ($2OCH_3$), 103.91 ($2C_{Ar}$), 107.88 (C_{Ar}), 108.62 (C_{Ar}), 117.47 (C_{Ar}), 119.72 (C_{Ar}), 126.79 (C_{Ar}), 133.34 (C_{Ar}), 133.60 (C_{Ar}), 157.60 (C_{Het}), 158.90 (C_{Het}), 160.02 ($2C_{Ar}$), 164.89 (C_{Ar}). Found, %: C 64.46; H 4.75; N 9.44. $C_{16}H_{14}N_2O_4$. Calculated, %: C 64.42; H 4.73; N 9.39.

2-(2,6-Dimethoxyphenyl)-5-(2-methoxyphenyl)-1,3,4-oxadiazole (3c) was prepared in a similar manner by the cyclization of benzohydrazide **2c** in thionyl chloride. Yield 1.72 g (69%), colorless crystals, mp 138–140°C. IR spectrum, ν, cm^{-1}: 753, 771, 789, 807, 965, 982, 1010, 1043, 1128, 1166, 1244, 1266, 1283, 1439, 1456, 1468; 1487; 1554, 1565, 1598 (C=C); 1617, 1641 (C=N). UV spectrum, λ_{max}, nm [$\varepsilon\times10^{-4}$ L mol^{-1} cm^{-1}, λ_{exc} 300 nm]: isooctane, 257 [1.16], 285 [0.81], 297 [0.75], λ^{fl}_{max} (φ) 352 (0.16) ; acetonitrile, 254 [1.37], 287 [0.88], 297 [0.79], λ^{fl}_{max} (φ) 357 (0.15); DMSO, 288 [1.16], 300 [1.05], λ^{fl}_{max} (φ) 363 (0.33). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.79 s (6H, 2,6-OCH_3), 3.95 s (3H, OCH_3), 6.61 d (2H, H_{Ar}, J = 8.4 Hz), 6.99–7.11 m (2H, H_{Ar}), 7.36–7.53 m (2H, H_{Ar}), 7.95 d.d (1H, H_{Ar}, J_1 = 1.8, J_2 = 7.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 56.09 ($2OCH_3$), 56.10 (OCH_3), 103.17 (C_{Ar}), 103.90 ($2C_{Ar}$), 111.98 (C_{Ar}), 113.61 (C_{Ar}), 120.65 (C_{Ar}), 130.61 (C_{Ar}), 132.71 (C_{Ar}), 133.24 (C_{Ar}), 157.93 (C_{Het}), 159.16 (C_{Het}), 159.98 ($2C_{Ar}$), 163.86 (C_{Ar}). Found, %: C 65.44; H 5.13; N 9.04. $C_{17}H_{16}N_2O_4$. Calculated, %: C 65.38; H 5.16; N 8.97.

IR spectra were recorded on a Varian Excalibur 3100 FT-IR spectrometer in Nujol. ^{1}H (250.13 MHz) and ^{13}C (62.90 MHz) NMR spectra were obtained on a Bruker DPX-250 instrument. The absorption and fluorescence spectra were measured on a Cary Scan 100 spectrophotometer and a Cary Eclipse fluorescence spectrophotometer, respectively. The fluorescence quantum yields were determined relative to anthracene in acetonitrile [17].

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