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LETTERS TO THE EDITOR

Spectral-Luminescent Properties of 2-Aryl-1,3,4-oxadiazoles

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Abstract—Refluxing equimolar amounts of acylhydrazides with triethyl orthoformate in *o*-xylene yielded 2-aryl-1,3,4-oxadiazoles luminescing with high quantum yields in polar and nonpolar solvents (λ_{max}^{fl} 299–349 nm, φ 0.20–0.62). The only exception was 2-(1,3,4-oxadiazol-2-yl)phenol emitting intensely only in highly polar aprotic DMSO (λ_{max}^{fl} 350 nm, φ 0.19).

Keywords: 2-aryl-1,3,4-oxadiazoles, luminescence, quantum luminescence yield, organic phosphors

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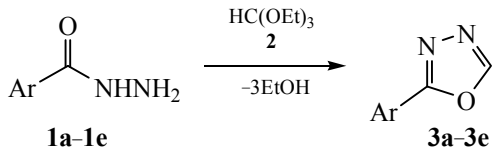
1,3,4-Oxadiazoles and their derivatives exhibit high and diverse biological activity [1], good electron-conducting properties, intense luminescence in the short-wave region of visible spectrum [2], and high thermal and chemical stability, which makes them widely applicable in various areas of agro- [3] and medical chemistry [4], as well as in production of highly effective organic and metal complex phosphors [5–7]. For expanding the range of such compounds of this class and for studying their spectral-luminescent properties we employed herein refluxing equimolar amounts of acylhydrazides **1a–1e** with triethyl orthoformate **2** in *o*-xylene to obtain 2-aryl-1,3,4-oxadiazoles **3a–3e** (Scheme 1).

In the absorption spectra of oxadiazoles **3a–e**, the maximum of the long-wave band due to $S_0 \rightarrow S_1$ electronic $\pi \rightarrow \pi^*$ transitions in conjugated 1,3,4-oxadiazole and aryl moieties occurs in the 246–308 nm region. The luminescence spectra of oxadiazole **3b** in isooctane and acetonitrile contain two bands: a short-wave band (λ_{max}^{fl} 335, 357 nm, φ 0.001, 0.04) with normal (3044, 4457 cm^{-1}) and a long-wave band (λ_{max}^{fl} 470, 491 nm, φ 0.002, 0.003) with anomalously high (11618, 12191 cm^{-1}) Stokes shift.

Based on the fluorescence excitation spectra, the short-wave luminescence band was assigned to the initial benzenoid structure of **3b**, and the long-wave luminescence was associated with emission of a short-lived phototautomer resulted from an excited-state intramolecular proton transfer (ESIPT) from the phenolic OH group to the nearest heterocyclict nitrogen atom [8, 9]. A strong intramolecular hydrogen bond O–H···N between the *ortho*-phenolic hydroxy group and the oxadiazole ring favors photoinitiated proton transfer in oxadiazole **3b**, as confirmed by IR [ν(OH) 3203 cm^{-1}] and ^{1}H NMR [δ(OH) 10.03 ppm] spectroscopic data A low total luminescence quantum yield exhibited by oxadiazole **3b** (φ 0.003, 0.043) is due to nonradiative deactivation of its excited state by the ESIPT mechanism [10]. However, in highly polar DMSO the spectrum of oxadiazole **3b** contains only one short-wave high-intensity band (λ_{max}^{fl} 350 nm, φ 0.19) with a normal Stokes shift (4324 cm^{-1}), assigned to the initial benzenoid structure of **3b** based on the fluorescence

Scheme 1.



1a–1e **3a–3e**

Ar = Ph (**a**), 2-HOC_6H_4 (**b**), 2-$MeOC_6H_4$ (**c**), 3,4,5-$(MeO)_3C_6H_2$ (**d**), 3,4,5-$(EtO)_3C_6H_2$ (**e**).

excitation spectra. This is explained by strong intermolecular hydrogen bonding between the phenolic OH group of oxadiazole **3b** and highly polar aprotic DMSO, inhibiting the ESIPT process. A similar spectral behavior was previously observed in a structurally close compound, 2-(5-methyl-1,3,4-oxadiazol-2-yl)phenol [11]. Oxadiazoles **3a, 3c–3e**, in which the ESIPT is impossible because of the absence of a mobile proton, emit intensely in a closely adjacent spectral region (λ_{max}^{fl} 299–349 nm, φ 0.20–0.62). Their emission spectra exhibited a bathochromic shift of the luminescence maximum with increasing polarity of the solvent (by 2–20 nm) and also with accumulation of electron-donating substituents in the aryl ring (by 8–42 nm).

Thus, 2-aryl-1,3,4-oxadiazoles **3a, 3c–3e** exhibit intense luminescence in the short-wavelength region of the visible spectrum, which allows including these compounds among widely demanded violet-emitting organic phosphors. At the same time, oxadiazole **3b** containing a 2-hydroxyphenyl substituent in position 2 of the oxadiazole ring exhibits intense luminescence only in highly polar aprotic DMSO, while in other solvents its total luminescence quantum yield is low due to intramolecular proton transfer (ESIPT).

2-Phenyl-1,3,4-oxadiazole (3a). To a solution of 1.36 g (0.01 mol) of benzohydrazide **1a** in 50 mL of anhydrous o-xylene, 1.7 mL (0.01 mol) of triethyl orthoformate **2** in 10 mL of anhydrous *o*-xylene was added in small portions at room temperature with stirring. The reaction mixture was refluxed for 4–8 h (TLC control). The solvent was removed in a vacuum, and the product was isolated by column chromatography on silica gel (0.063–0.200 mm, eluent ethyl acetate-petroleum ether, 1 : 10), with the R_f 0.85 fraction being collected. Yield 1.02 g (70%), colorless liquid (cf. [12]). The IR and ^{1}H and ^{13}C NMR spectroscopic data for **3a** were consistent with those reported in [12]. UV spectrum, λ_{max}^{fl}, nm (ε× 10^{-4} L mol^{-1} cm^{-1}, λ_{exc} 245 nm): isooctane, 201 (0.92), 246 (0.68), λ_{max}^{fl} 299 (φ 0.20); acetonitrile, 201 [0.65], 246 [0.56], λ_{max}^{fl} 301 (φ 0.25).

2-(1,3,4-Oxadiazol-2-yl)phenol (3b) was prepared in a similar manner from salicylic acid hydrazide **1b.** Yield 1.08 g (67%), colorless crystals, mp 135–137°C (propan-2-ol) (mp 136–138°C [13]). The IR and ^{1}H and ^{13}C NMR spectroscopic data for **3b** were consistent with those reported in [13]. UV spectrum, λ_{max}, nm (ε×10^{-4} L mol^{-1} cm^{-1}, λ_{exc} 245 nm): isooctane, 245 (1.57), 250 (1.84), 255 (1.60), 261 (1.37), 307 (0.82), 318 (0.71), λ_{max}^{fl} 357 (φ 0.001), 491 (φ 0.002); acetonitrile, 212 (1.53), 249 (0.92), 260 (0.64), 304 (0.39), λ_{max}^{fl} 335 (φ 0.04), 470 (φ 0.003); DMSO, 304 (0.87), λ_{max}^{fl} 350 (φ 0.19).

2-(2-Methoxyphenyl)-1,3,4-oxadiazole (3c) was prepared in a similar manner from *o*-methoxybenzoic acid hydrazide **1c.** Yield 1.28 g (79%), light yellow crystals, mp 56–58°C (propan-2-ol) (mp 50–52°C [14]). The IR and ^{1}H and ^{13}C NMR spectroscopic data for **3c** were consistent with those reported in [14]. UV spectrum, λ_{max}, nm (ε×10^{-4} L mol^{-1} cm^{-1}, λ_{exc} 245 nm): isooctane, 211 (2.14), 246 (1.12), 296 (0.62), 308 (0.34), λ_{max}^{fl} 326 φ 0.52); acetonitrile, 210 (2.63), 245 (1.28), 296 (0.58), λ_{max}^{fl} 336 (φ 0.42); DMSO, 298 (0.38), 311 (0.25), λ_{max}^{fl} 341 (φ 0.40).

2-(3,4,5-Trimethoxyphenyl)-1,3,4-oxadiazole (3d) was prepared in a similar manner from 3,4,5-trimethoxybenzoic acid hydrazide **1d** [15]. Yield 1.70 g (75%), colorless crystals, mp 137–138°C (propan-2-ol) (mp 138–139°C [16]). IR spectrum, ν, cm^{-1}: 768, 837, 855, 966, 998, 1073, 1103, 1122, 1172, 1247 (C–O–C), 1339, 1368, 1509, 1558 (C=C), 1590 (C=N), 3075. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.90 s (3H, 4-OCH_3), 3.92 s [6H, 3,5-$(OCH_3)_2$], 7.30 s (2H, H_{Ar}), 8.42 s (1H, H_{Het}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 56.59 (2OCH_3), 60.68 (OCH_3), 105.76 (2C_{Ar}), 126.18 (2C_{Ar}), 141.65 (C_{Ar}), 153.32 (C_{Het}), 153.94 (C_{Ar}), 165.54 (C_{Het}). UV spectrum, λ_{max}, nm (ε×10^{-4} L mol^{-1} cm^{-1}, λ_{exc} 245 nm): isooctane, 211 (1.54), 275 (0.63), 293 (0.34), λ_{max}^{fl} 329 (φ 0.36); acetonitrile, 216 (3.54), 270 (1.26), 291 (0.63), λ_{max}^{fl} 343 (φ 0.35); DMSO, 276 (1.03), 297 (0.54), λ_{max}^{fl} 349 (φ 0.21).

2-(3,4,5-Triethoxyphenyl)-1,3,4-oxadiazole (3e) was prepared in a similar manner from 3,4,5-triethoxybenzoic acid hydrazide **1e** [17]. Yield 1.95 g (70%), colorless crystals, mp 133–135°C (propan-2-ol). IR spectrum, ν, cm^{-1}: 743, 764, 787, 831, 852, 889, 904, 956, 968, 1037, 1108, 1125, 1222, 1242 (C–O–C), 1284, 1294, 1354, 1496, 1513, 1554 (C=C), 1591 (C=N), 3089. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (3H, 4-CH_3, J = 7.5 Hz), 1.38 t [6H, 3,5-$(CH_3)_2$, J = 7.5 Hz], 4.07 q [6H, 3.4.5-$(OCH_2)_3$, J = 7.5 Hz], 7.19 s (2H, H_{Ar}), 8.46 s (1H, H_{Het}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.74 (2CH_3), 15.52 (CH_3), 64.77 (2OCH_2), 68.97 (OCH_2), 105.44 (2C_{Ar}), 118.14 (2C_{Ar}), 141.02 (C_{Ar}), 152.99 (C_{Ar}), 153.31 (C_{Het}), 164.65 (C_{Het}). UV spectrum, λ_{max}, nm (ε×10^{-4} L mol^{-1} cm^{-1}, λ_{exc} 245 nm): isooctane, 221 (2.71), 274 (1.27), λ_{max}^{fl} 331 (φ 0.37); dioxane, 276 (1.62), λ_{max}^{fl} 339 (φ 0.55);

acetonitrile, 221 (3.82), 275 (1.73), 296 (0.58), λ_{max}^{fl} 336 (φ 0.62). Found, %: C 60.58; H 6.47; N 10.53. $C_{14}H_{18}N_2O_4$. Calculated, %: C 60.42; H 6.52; N 10.66.

IR spectra were recorded on a Varian Excalibur 3100 FT-IR spectrometer in Nujol. ^1H (250.13 MHz) and ^{13}C (62.90 MHz) NMR spectra were obtained on a Bruker DPX-250 instrument. 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 [18].

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