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SHORT COMMUNICATIONS

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

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Abstract—Reaction of aroylhydrazides with 2,4,6-trimethylbenzoyl chloride in the presence of Et_3N afforded N-(mesityl)aroylhydrazides, which through subsequent cyclization at treatment with $SOCl_2$ resulted in 2-aryl-5-(2,4,6-trimethylphenyl)-1*H*-1,3,4-oxadiazoles. For 2-hydroxyphenyl derivative containing a stable O–H N intramolecular bond a low quantum luminescence yield is observed (φ 0.006–0.038) due to the nonradiative deactivation of the agitated state by ESPIT mechanism.

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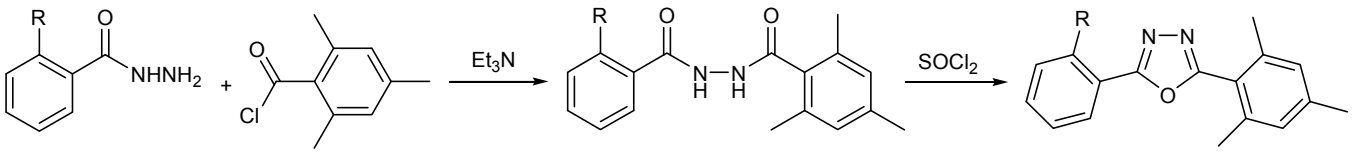
2,5-Diaryl-1,3,4-oxadiazoles possess a wide range of versatile biological activity [1], and also interesting photophysical properties [2] that allow making on their basis organic [3, 4] and metal complex [5] luminophores, capable of effective radiation in a shortwave region of visible spectrum [6]. In this connection extending the range of such compounds and exploring their spectral luminescent properties is an actual task.

To this end we prepared by the reaction of hydrazides **1a–1c** with 2,4,6-trimethylbenzoyl chloride in the presence of triethylamine benzoylbenzohydrazides **2a–2c**, which at subsequent cyclization with thionyl chloride afforded 2-aryl-5-(2,4,6-trimethylphenyl)-1*H*-1,3,4-oxadiazoles **3a–3c**.

In absorption spectra of oxadiazoles **3a–3c** a maximum of longwave band is observed at 261–311 nm which is due to π→π* electron transitions indicating the existence of these compounds in solutions as benzoic structures of type **3**. IR and ^1H NMR spectra of oxadiazoles **3a–3c** are consistent with their benzoic structures, and in the case of compound **3b** they indicate the presence of a stable intramolecular hydrogen bond between *ortho*-phenol hydroxy group and the nearest nitrogen atom of the azole ring (O–H N). Namely, in the IR spectrum of 2-(2-hydroxyphenyl)-5-(2,4,6-trimethylphenyl)-1*H*-1,3,4-oxadiazole **3b** a wide band of OH group absorption is present at 3439 cm^{-1} typical of intramolecular hydrogen bonds that is absent in compounds **3a** and **3c**. More than that, the presence of a stable intramolecular hydrogen bond O–H N in oxadiazole **3b** is indicated by the shift of the stretching vibrations of the $C^2{=}N^3$ bond (1627 cm^{-1}) to the region of low frequencies by 20 and 13 cm^{-1} as compared to



1a–1c **2a–2c** **3a–3c**

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

similar absorption in IR spectra of oxadiazoles **3a** (1647 cm^{-1}) and **3c** (1640 cm^{-1}), in which this interaction is not present. In ^1H NMR spectrum of oxadiazole **3b** in $CDCl_3$ a downfield shift of the signal of the hydroxy group proton (10.31 ppm) is observed that also evidences the presence of a stable intramolecular hydrogen bond.

In the luminescence spectra of oxadiazole **3b** two bands are present: a shortwave (λ_{max}^{fl} 354–397 nm, φ 0.002–0.035) with a normal (4219–6965 cm^{-1}) and a longwave (λ_{max}^{fl} 476–491 nm, φ 0.001–0.004) with abnormally high (11460–12081 cm^{-1}) Stocks shift. By fluorescence excitation spectra the shortwave luminescence was assigned to the initial benzoic structure **3b**, and the longwave band, to the emission of short-lived phototautomer resulting from a proton transfer in the excited state from phenol hydroxyl to the nitrogen atom of oxadiazole bound to it with the intramolecular hydrogen bond by ESIPT mechanism (excited-state intramolecular proton transfer) [7, 8]. The low summary quantum yield of oxadiazole **3b** luminescence (φ 0.006–0.038) is caused by the nonradiative deactivation of its excited state by ESIPT mechanism. Previously such effects were discovered in spectra of *ortho*-hydroxyphenyl-1,3,4(1,2,4)-oxadiazoles [9–11] and 1,2,4-triazoles [12] structurally similar to compound **3b**.

In 2-phenyl- and 2-(2-methoxyphenyl)derivatives **3a** and **3c** the ESIPT process is impossible due to the lack of mobile proton of *ortho*-phenol hydroxy group in its molecules; as a result in their luminescence spectra only one highly intensive shortwave luminescence band (λ_{max}^{fl} 349–360 nm, φ 0.30–0.98) is present that undergoes slight shift into the red region with increasing solvent polarity (5–6 nm), and also with electron-donor character of the aryl substituent in the position *2* of oxadiazole ring (by 2–4 nm). The highest quantum luminescence yield for compounds **3a** and **3c** is observed in acetonitrile (φ 0.86, 0.98), and the lowest, in DMSO (φ 0.30, 0.68). Such effects are also observed in the spectra of 8-hydroxy-2-styrylquinolines at substitution of mobile proton of phenol group by methyl or benzyl substituent [13, 14]. As a result, as in the case of **3a** and **3c**, a significant increase in the luminescence quantum yield occurs in the corresponding alkyl derivatives compared to initial compounds.

Hence, the replacement of the *ortho*-phenol substituent in 2-(2-hydroxyphenyl)-5-(2,4,6-trimethylphenyl)-1*H*-1,3,4-oxadiazol **3b** by phenyl or *ortho*-methoxyphenyl group blocks the ESIPT process in oxadiazoles **3a** and **3c**. As a result they show a strong radiation in the shortwave region of visible spectrum with spectral luminescent characteristics, allowing classing them among widely popular organic luminophores of oxadiazole series.

***N'*-Benzoyl-2,4,6-trimethylbenzohydrazide (2a).** To solution of 1.36 g (10 mmol) of benzohydrazide **1a** in 20 mL of dried acetonitrile at stirring was added in succession 5 mL of triethylamine and 2.01 g (11 mmol) of 2,4,6-trimethylbenzoyl chloride in 30 mL of dried acetonitrile. The reaction mixture was left for 24 h at room temperature and afterwards it was boiled for 3 h. The solvent was removed in a vacuum, oily residue was washed with water (2 × 10 mL), dried in air, the reaction product was isolated by column chromatography on silica gel (0.063–0.200 mm, eluent ethyl acetate–petroleum ether, 1 : 2), collecting fraction with R_f 0.75. After distilling off the solvent the residue was recrystallized from 2-propanol (2 × 15 mL). Yield 2.40 g (85%), colorless crystals, mp. 203–204°C (mp. 202–205°C [15, 16]). IR spectrum (KBr), ν, cm^{-1}: 3240, 3174 (NH); 1685, 1637 (C=O); 1616, 1599 (C=C); 1551, 1516, 1489, 1461, 1448, 1379, 1259, 1243, 1170, 1103, 1070, 1027, 1002, 986, 847, 784, 782. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.28 s (3H, 4-CH_3), 2.35 s (6H, 2,6-CH_3), 6.86 s (2H_{arom}), 7.48 d.d (2H_{arom}, J_1 7.9, J_2 7.5 Hz), 7.52 d.d (1H_{arom}, J_1 7.5, J_2 1.4 Hz), 7.83 d.d (2H_{arom}, J_1 7.9, J_2 1.5 Hz), 8.63 d (1H, NH, *J* 2.5 Hz), 9.45 d (1H, NH, *J* 2.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 19.92 (2,6-CH_3), 21.16 (4-CH_3), 123.85 ($C_{arom.quat.}$), 126.89 (C_{arom}), 128.24 (2C_{arom}), 129.12 (C_{arom}), 131.55 ($C_{arom.quat.}$), 131.82 (C_{arom}), 135.11 (2$C_{arom.quat.}$), 139.21 ($C_{arom.quat.}$), 168.33 (C=O), 173.34 (C=O). Found, %: C 72.25; H 6.44; N 9.97. $C_{17}H_{18}N_2O_2$. Calculated, %: C 72.32; H 6.43; N 9.92.

***N'*-(2-Hydroxybenzoyl)-2,4,6-trimethylbenzohydrazide (2b)** was obtained similarly from hydrazide of salicylic acid **1b**. Yield 2.33 g (78%), colorless crystals, mp. 140–142°C. IR spectrum (KBr), ν, cm^{-1}: 3421 (OH); 3294, 3270 (NH); 1685, 1654 (C=O); 1640, 1613, 1598 (C=C); 1540, 1490, 1488, 1378, 1350, 1291, 1257, 1215, 1162, 1151, 1103, 1050, 1035, 979, 951, 889, 847, 828. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.46 s (3H, 4-CH_3), 2.54 s (6H, 2,6-CH_3), 7.10 s (2H_{arom}), 7.14–7.23 m (2H_{arom}), 7.67 d.d (1H_{arom}, J_1 7.6, J_2 7.5 Hz), 8.18 d.d (1H_{arom}, J_1 7.6, J_2 7.5 Hz), 10.28 d (1H, NH, *J* 4.5 Hz), 10.88 d (1H, NH, *J* 4.5 Hz), 12.31 s (1H, OH). ^{13}C NMR spectrum

(DMSO-d_6), δ, ppm: 19.42 (2,6-CH_3), 21.34 (4-CH_3), 114.47 ($C_{arom.quat.}$), 117.91 (C_{arom}), 119.46 (C_{arom}), 128.21 ($2C_{arom}$), 128.69 (C_{arom}), 133.68 ($C_{arom.quat.}$), 134.12 (C_{arom}), 134.94 ($2C_{arom.quat.}$), 138.11 ($C_{arom.quat.}$), 160.05 ($C_{arom.quat.}$), 168.53 (C=O), 168.94 (C=O). Found, %: C 68.49; H 6.05; N 9.42. $C_{17}H_{18}N_2O_3$. Calculated, %: C 68.44; H 6.08; N 9.39.

2,4,6-Trimethyl-*N'*-(2-methoxybenzoyl)benzohydrazide (2c) was obtained similarly from hydrazide **1c**. Yield 2.53 g (81%), colorless crystals, mp. 160–162°C. IR spectrum (KBr), ν, cm^{-1}: 3321, 3233 (NH); 1689, 1636 (C=O); 1634, 1611, 1600, 1577 (C=C); 1508, 1507, 1484, 1470, 1460, 1434, 1317, 1294, 1250, 1183, 1157, 1120, 1018, 851. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.24 s (3H, 4-CH_3), 2.33 s (6H, 2,6-CH_3), 4.08 s (3H, OCH_3), 6.82 s ($2H_{arom}$), 6.98–7.06 m ($2H_{arom}$), 7.48 d.d ($1H_{arom}$, J_1 7.6, J_2 7.5 Hz), 7.92 d.d ($1H_{arom}$, J_1 7.6, J_2 7.5 Hz), 9.53 d (1H, NH, J 7.5 Hz), 10.87 d (1H, NH, J 7.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 19.56(2,6-CH_3), 21.45 (4-CH_3), 46.23 (OCH_3), 111.52 (C_{arom}), 118.69 ($C_{arom.quat.}$), 121.33 (C_{arom}), 128.36 ($2C_{arom}$), 132.30 ($C_{arom.quat.}$), 132.31 (C_{arom}), 133.88 (C_{arom}), 135.42 ($2C_{arom.quat.}$), 139.07 ($C_{arom.quat.}$), 157.76 ($C_{arom.quat.}$), 161.06 (C=O), 166.25 (C=O). Found, %: C 69.23; H 6.44; N 9.02. $C_{18}H_{20}N_2O_3$. Calculated, %: C 69.21; H 6.45; N 8.97.

2-(2,4,6-Trimethylphenyl)-5-phenyl-1*H*-1,3,4-oxadiazole (3a). A solution of 1.98 g (7 mmol) of hydrazide **2a** in 50 mL of thionyl chloride was boiled during 5 h, then thionyl chloride was distilledoff while heating on a water bath. Into the flask with oily residue 50 g of crushed ice was added, the precipitate was filtered off, washed it with cold water (2 × 30 mL), dried in open air, and purified by column chromatography (eluent ethylcetate–petroleum ether, 1 : 5), fraction was collected with R_f 0.75–0.80. After distilling off the solvent the residue was recrystallized from 2-propanol. Yield 1.02 g (55%), colorless crystals, mp. 93–94°C (mp. 92–94°C [15], 95–96°C [16]). IR spectrum (KBr), ν, cm^{-1}: 1647, 1610 (C=N); 1590, 1567 (C=C); 1551, 1512, 1482, 1456, 1448, 1352, 1261, 1247, 1167, 1098, 1071, 1049, 1024, 964, 867, 850, 779, 752. UV spectrum, λ_{max}, nm [$\varepsilon\cdot10^{-4}$ L/(mol·cm), λ_{excit} 300 nm]: toluene, 290 [1.56], λ_{max}^{fl} (φ) 352 (0.84); acetonitrile, 261 [2.70], λ_{max}^{fl} (φ) 349 (0.98); DMSO, 264 [1.88], λ_{max}^{fl} (φ) 358 (0.30). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.31 s (6H, 2,6-CH_3), 2.33 s (3H, 4-CH_3), 6.96 s ($2H_{arom}$), 7.47–7.54 m ($3H_{arom}$), 8.06–8.15 m ($2H_{arom}$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 20.90 (2C, 2,6-CH_3), 21.68 (4-CH_3), 121.56 ($C_{arom.quat.}$), 124.52 ($C_{arom.quat.}$), 127.28 (2C, C_{arom}), 129.31 (2C, C_{arom}), 129.51 ($2C_{arom}$), 132.08 (C_{arom}), 139.17 ($2C_{arom.quat.}$), 141.45 ($C_{arom.quat.}$), 164.35 ($C_{Ht,quat.}$), 165.26 ($C_{Ht,quat.}$). Found, %: C 77.31; H 6.12; N 10.57. $C_{17}H_{17}N_2O$. Calculated, %: C 77.25; H 6.10; N 10.60.

2-[5-(2,4,6-Trimethylphenyl)-1*H*-1,3,4-oxadiazol-2-yl]phenol (3b) was obtained similarly. Yield 0.94 g (48%), colorless crystals, mp. 92–94°C. IR spectrum (KBr), ν, cm^{-1}: 3439 (OH); 1627, 1614 (C=N); 1595, 1591 (C=C); 1559, 1545, 1516, 1507, 1489, 1383, 1359, 1259, 1256, 1238, 1211, 1148, 1049, 1032, 975, 850, 846, 745. UV spectrum, λ_{max}, nm [$\varepsilon\cdot10^{-4}$, L/(mol·cm), λ_{excit} 300 nm]: isooctane, 202 [8.30], 264 [3.39], 311 [2.43], λ_{max}^{fl} (φ) 397 (0.002), 491 (0.004); acetonitrile, 258 [2.59], 308 [1.72], λ_{max}^{fl} (φ) 354 (0.005), 476 (0.001); DMSO, 307 [0.93], λ_{max}^{fl} (φ) 365 (0.035), 488 (0.003). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.39 s (6H, 2,6-CH_3), 2.42 s (3H, 4-CH_3), 7.03–7.11 m ($3H_{arom}$), 7.21 d ($1H_{arom}$, J 7.6 Hz), 7.51 d.d ($1H_{arom}$, J_1 7.6, J_2 7.5 Hz), 7.82 d ($1H_{arom}$, J 7.5 Hz), 10.31 s (1H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 20.56 (2C, 2,6-CH_3), 21.32 (4-CH_3), 108.27 ($C_{arom.quat.}$), 117.65 (C_{arom}), 120.21 (C_{arom}), 120.35 ($C_{arom.quat.}$), 126.58 (C_{arom}), 129.06 ($2C_{arom}$), 133.66 (C_{arom}), 138.91 ($2C_{arom.quat.}$), 141.47 ($C_{arom.quat.}$), 157.66 ($C_{arom.quat.}$), 163.29 ($C_{Ht,quat.}$), 164.85 ($C_{Ht,quat.}$). Found, %: C 72.83; H 5.77; N 10.03. $C_{17}H_{16}N_2O_2$. Calculated, %: C 72.84; H 5.75; N 9.99.

2-[(2,4,6-Trimethylphenyl)-5-(2-methoxyphenyl)]-1*H*-1,3,4-oxadiazole (3c) was obtained similarly. Yield 1.28 g (62%), colorless crystals, mp. 60–62°C. IR spectrum (KBr), ν, cm^{-1}: 1640, 1607 (C=N); 1591, 1572 (C=C); 1543, 1475, 1472, 1437, 1350, 1278, 1266, 1182, 1159, 1053, 1041, 1024, 968, 863, 771, 756. UV spectrum, λ_{max}, nm [$\varepsilon\cdot10^{-4}$, L/(mol·cm), λ_{excit} 300 nm]: toluene, 305 [0.88], λ_{max}^{fl} (φ) 355 (0.69); acetonitrile, 255 [1.80], 298 [0.86], λ_{max}^{fl} (φ) 353 (0.86); DMSO, 302 [0.87], λ_{max}^{fl} (φ) 360 (0.68). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.32 s (9H, 2,4,6-CH_3), 3.95 s (3H, OCH_3), 6.96 s ($2H_{arom}$), 7.03–7.11 m ($2H_{arom}$), 7.49 d.d ($1H_{arom}$, J_1 7.6, J_2 7.5 Hz), 7.98 d.d ($1H_{arom}$, J_1 7.5, J_2 2.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 20.94 (2,6-CH_3), 21.67 (4-CH_3), 56.35 (OCH_3), 112.20 (C_{arom}), 113.67 ($C_{arom.quat.}$), 121.18 (C_{arom}), 121.76 ($C_{arom.quat.}$), 129.26 ($2C_{arom}$), 130.81 (C_{arom}), 133.37 (C_{arom}), 139.26 ($2C_{arom.quat.}$), 141.19 ($C_{arom.quat.}$), 158.30 ($C_{arom.quat.}$), 164.10 ($C_{Ht,quat.}$), 164.07 ($C_{Ht,quat.}$). Found, %: C 73.41; H 6.18; N 9.48. $C_{18}H_{18}N_2O_2$. Calculated, %: C 73.45; H 6.16; N 9.52.

IR spectra were registered on a spectrophotometer Varian Excalibur 3100 FT-IR, ^{1}H (250.13 MHz), ^{13}C (62.90 MHz) NMR spectra were recorded on an instrument Bruker DPX-250. Absorption and fluorescent spectra were measured on a spectrophotometer Cary Scan 100 and a spectrofluorimeter Cary Eclipse respectively. Quantum yields of fluorescence were determined with respect to the acetonitrile solution of anthracene [11].

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