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LETTERS TO THE EDITOR

Synthesis and Luminescent Properties of 2-[2'-Acyl(benzoyl)oxyphenyl]-5-(4''-nonylphenyl)-1,3,4-oxadiazole

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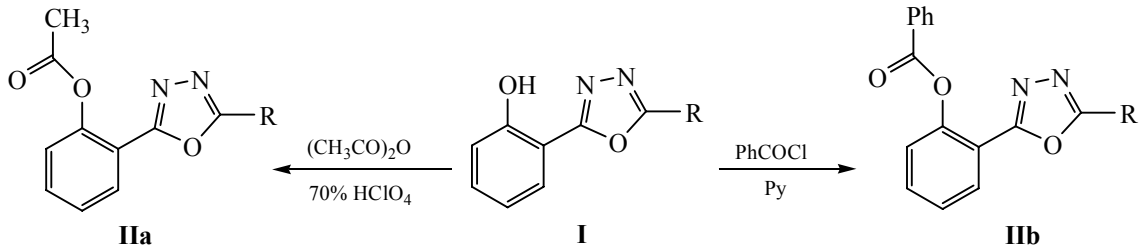
Organic phosphorus based on 2,5-diaryl-1,3,4-oxadiazoles are widely used as optical brighteners, activating additives to liquid and plastic scintillation detectors [1], heterocyclic ligands for electroluminescent metal complexes in the preparation of highly emissive and electron-transport materials for organic light-emitting diodes (OLEDs) [2–4], the active media for tunable lasers based on phosphorus [5]. In this regard, the synthesis of these compounds and the study of their photophysical properties is an important task.

For this purpose, we obtained acyl derivative **IIa** by acylation of 2-(2'-hydroxyphenyl)-5-(4''-nonylphenyl)-1,3,4-oxadiazole **I** [6] with acetic anhydride in the presence of a catalytic amount of 70% perchloric acid, and benzoyl derivative **IIb** by the action of benzoyl chloride in pyridine (Scheme 1).

The structure of oxadiazoles **IIa** and **IIb** suggests that they may have interesting luminescent properties that have been studied in this work, and the presence in of long-chain alkyl groups increases their solubility in organic solvents. In addition, these substituents can impart mesogenic properties to these compounds, which is of a separate interest.

We have previously prepared benzoyl derivatives of 2-(2'-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazole **IIIa** and 2-(2'-hydroxyphenyl)-5-(3'',4'',5''-trimethoxyphenyl)-1,3,4-oxadiazole **IIIb**, whose solutions in toluene, CH_3CN or DMSO emit in the violet region of the visible spectrum (λ_{max}^{fl} 338–433 nm) [7]. The luminescence quantum yield of oxadiazole **IIIa** was quite low (φ 0.032–0.087) since their singlet and triplet *n*–π*-levels lie obviously below the corresponding

Scheme 1.



IIa **I** **IIb**

R = 4-$C_9H_{19}C_6H_4$.

π–π*-states owing to the presence of the carbonyl group as in the case of benzoyl ester of 8-hydroxyquinoline [8]. Therefore the probability of intercombination conversions leading to nonradiative deactivation of its excited state increases [1]. The introduction of three electron-donating methoxy substituents into the 5-aryl moiety changes the relative positions of *n*–π*- and π–π*-levels by reducing their energy and increases significantly the luminescence quantum yield of oxadiazole **IIIb** (φ 0.11–0.51). This effect could not be fully attained in the case of oxadiazole **IIb** containing an alkyl substituent at the 5-aryl ring, although its luminescence quantum yield increased slightly (λ_{max}^{fl} 341–360 nm, φ 0.036–0.098) as compared with compound **IIIa**. A significant increase in the luminescence quantum yield of oxadiazole **I** derivatives was obtained by replacing the benzoyl group with acyl moiety and by increasing the energy of *n*–π*-levels in **IIa** (acetonitrile, λ_{max}^{fl} 353 nm, φ 0.91; isooctane , λ_{max}^{fl} 351 nm, φ 0.95). It should be noted that oxadiazole **I** luminesces with a low quantum yields (λ_{max}^{fl} 350–503 nm, φ 0.008–0.012) [6], which is caused by nonradiative deactivation of its excited state by ESIPT-mechanism [9, 10].

Hence, the replacement of 2'-benzoyloxy fragment with 2'-acyloxy group in 2,5-diaryl-1,3,4-oxadiazole leads to a significant increase in the luminescence quantum yield and opens the possibility of obtaining a wide range of new effective organic phosphorus, which can be required in the designing and production of various photo- and electroluminescent devices.

The procedure for the preparation of 2-(2'-hydroxyphenyl)-5-(4"-nonylphenyl)-1,3,4-oxadiazole **I** and its properties have been we described in [6]. Structures of its acyl (**IIa**) and benzoyl (**IIb**) derivatives were established by IR, UV, ^{1}H, ^{13}C NMR spectroscopy and elemental analysis data.

{2-[5-(4-Nonylphenyl)-1,3,4-oxadiazol-2-yl]phenyl}-acetate (IIa). A suspension of 0.48 g (0.001 mol) of oxadiazole **I** in 2 mL of acetic anhydride and two drops of 70% perchloric acid was heated with stirring until azole dissolved. The reaction mixture was kept for 10 h at room temperature, and then diluted with water (30 mL). The precipitate was filtered off, washed with water (2 × 10 mL), and dried in a vacuum. The product was recrystallized from *n*-hexane (2 × 30 mL). Yield 0.28 g (70%), colorless crystals, mp 69–70°C. IR spectrum, ν, cm^{-1}: 1560 (C=C, C=N), 1585, 1613, 1756 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.87 t (3H, CH_3, $^3J_{HH}$ 7.5 Hz), 1.26–1.32 m (12H, CH_2), 1.64 q (2H, CH_2, $^3J_{HH}$ 7.5 Hz), 2.39 s (3H, CH_3CO), 2.67 t (2H, CH_2, $^3J_{HH}$ 7.6 Hz), 7.26–7.66 m (5H, H_{Ar}), 7.97 d (2H, H_{Ar}, $^3J_{HH}$ 10.1 Hz), 8.13 d (1H, H_{Ar}, $^3J_{HH}$ 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.12 (CH_3), 21.29 ($\underline{C}H_3CO$), 22.68 (CH_2), 29.26 (CH_2), 29.31 (CH_2), 29.47 (CH_2), 29.53 (CH_2), 31.12 (CH_2), 31.88 (CH_2), 36.00 (CH_2), 117.65 (C_{Ar}), 119.86 (C_{Ar}, C_{quart}), 121.07 (C_{Ar}), 124.20 (C_{Ar}), 126.51 (C_{Ar}), 126.90 ($2C_{Ar}$), 129.19 ($2C_{Ar}$), 132.59 (C_{Ar}, C_{quart}), 147.46 (C_{Ar}, C_{quart}), 148.78 (C_{Ar}, C_{quart}), 161.47 (C_{Het}, C_{quart}), 164.34 (C_{Het}, C_{quart}), 169.69 (C=O, C_{quart}). UV spectrum, λ_{max}, nm [ε·10^{-4}, L mol^{-1} cm^{-1}, λ_{ex} 300 nm]: isooctane, λ_{max} 206 (2.69), 285 (3.20), λ_{max}^{fl} 351, φ 0.95; acetonitrile, λ_{max} 283 (2.87), λ_{max}^{fl} 353, φ 0.91. Found, %: C 73.60; H 7.50; N 6.57. $C_{25}H_{30}N_2O_3$. Calculated, %: C 73.86; H 7.44; N 6.89.

{2-[5-(4-Nonylphenyl)-1,3,4-oxadiazol-2-yl]-phenyl}benzoate (IIb) was obtained similarly from 0.48 g (0.001 mol) of oxadiazole **I**, 1 mL of pyridine, and 0.25 mL (0.002 mol) of benzoyl chloride. Yield 0.26 g (55%), pale brown crystals, mp 70–72°C (*n*-hexane). IR spectrum, ν, cm^{-1}: 1540 (C=C, C=N), 1587, 1612, 1738 (C=O). ^{1}H NMR (DMSO-d_6), δ, ppm: 0.87 t (3H, CH_3, $^3J_{HH}$ 7.5 Hz), 1.15–1.35 m (12H, CH_2), 1.56 q (2H, CH_2, $^3J_{HH}$ 7.5 Hz), 2.60 t (2H, CH_2, $^3J_{HH}$ 7.6 Hz), 7.18 d (2H, H_{Ar}, $^3J_{HH}$ 5.1 Hz), 7.51–7.80 m (8H, H_{Ar}), 8.21–8.30 m (3H, H_{Ar}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.13 (CH_3), 22.68 (CH_2), 29.22 (CH_2), 29.31 (CH_2), 29.46 (CH_2), 29.53 (CH_2), 29.71 (CH_2), 31.12 (CH_2), 35.94 (CH_2), 117.82 (C_{Ar}, C_{qurt}), 120.92 (C_{Ar}, C_{quart}), 124.33 (C_{Ar}), 126.70 (C_{Ar}), 126.79 ($2C_{Ar}$), 128.76 ($2C_{Ar}$), 128.92 ($2C_{Ar}$), 129.28 (C_{Ar}, C_{quart}), 129.78 (C_{Ar}), 130.63 ($2C_{Ar}$), 132.73 (C_{Ar}), 133.86 (C_{Ar}), 147.17 (C_{Ar}, C_{quart}), 148.53 (C_{Ar}, C_{quart}), 161.87 (C_{Het}, C_{quart}), 164.80 (C_{Het}, C_{quart}), 165.72 (C=O, C_{quart}). UV spectrum, λ_{max}, nm [ε × 10^{-4}, L mol^{-1} cm^{-1}, λ_{ex} 300 nm]: isooctane, λ_{max} 229 (3.90), 283 (4.12), λ_{max}^{fl} 341, φ 0.098; acetonitrile, λ_{max} 225 (4.01), 282 (3.85), λ_{max}^{fl} 353, φ 0.036; DMSO, λ_{max} 286 (4.78), λ_{max}^{fl} 360, φ 0.038. Found, %: C 76.68; H 6.70; N 5.81. $C_{30}H_{32}N_2O_3$. Calculated, %: C 76.90; H 6.88; N 5.98.

IR spectra were recorded on a Varian Excalibur 3100 FT-IR spectrometer from a thin layer. ^{1}H (250.13 MHz) and ^{13}C NMR spectra (62.90 MHz) were recorded on a Bruker DPX-250. Absorption and fluorescence spectra were measured on a Cary Scan 100 spectrophotometer and a Cary Eclipse spectrofluorimeter, respectively. Fluorescence quantum yields were determined with respect to an acetonitrile solution of anthracene [5, 6].

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