ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 5, pp. 1074–1077. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © I.E. Mikhailov, D.A. Svetlichnyi, O.N. Burov, Yu.V. Revinskii, G.A. Dushenko, V.I. Minkin, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 5, pp. 776–780.

Synthesis and Spectral-Luminescence Properties of 2-[2-(Pyridin-4-yl)vinyl]quinolines

I. E. Mikhailov[a,b], D. A. Svetlichnyi[b], O. N. Burov[b], Yu. V. Revinskii[a], G. A. Dushenko[a,c], and V. I. Minkin[c]

[a] *Southern Scientific Center, Russian Academy of Sciences, ul. Chekhova 41, Rostov-on-Don, 344006 Russia e-mail: mikhail@ipoc.rsu.ru*

[b] *Southern Federal University, Rostov-on-Don, Russia*

[c] *Research Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, Russia*

Received December 29, 2014

Abstract—Condensation of 2-methylquinolines with 4-pyridinecarboxaldehyde in acetic acid anhydride has yielded 2-styryl-8-hydroxyquinoline along with its methyl and benzyl derivatives. Tosylation of 2-styryl-8-hydroxyquinoline has led to the corresponding *p*-toluenesulfonyloxy derivative. All the obtained compounds have revealed blue-green luminescence (λ_{max} = 438–512 nm); however, only alkyl derivatives of 2-styryl-8-hydroxyquinoline possessed the high quantum yield (φ = 0.16–0.41).

Keywords: 2-styryl-8-hydroxyquinoline, absorption spectrum, luminescence spectrum, quantum yield, organic luminophor

DOI: 10.1134/S1070363215050126

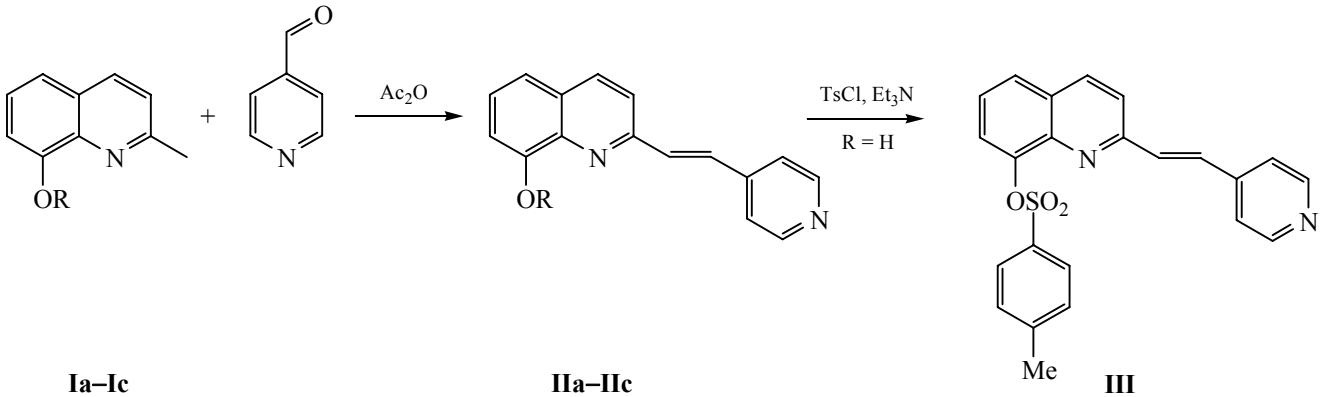
8-Hydroxyquinoline and its derivatives are among the universal ligands used in a wide range of practical applications [1]. They form stable complexes with majority of metals and they are often used as precipitants for separation of metal cations [2], highly selective fluorescent chemosensors [3], biologically active compounds [4], and components of efficient electroluminescent materials for organic light-emitting diodes (OLEDs) [5]. Fluorescence of 8-hydroxyquinoline is weak due to the photo-initiated excited-state intramolecular proton transfer (ESIPT) [6–8]; however, the proton transfer can be blocked via complexation with metal ions or the 8-hydroxyl group esterification, thus enhancing the fluorescence [9, 10]. Electronic π–π*-transfer in 8-hydroxyquinoline and its metal complexes significantly depends on the electronic parameters of the substituents in the quinoline ring; hence, fine tuning of the optical parameters as well as electronic and hole transport properties is possible via chemical modification of the ligand. Moreover, introduction of certain substituents (for instance, styryl) at the ligand enhances thermal stability of the metal–ligand complexes and their solubility in organic media [11, 12].

Aiming to expand a range of the above-mentioned compounds and study their luminescent properties, novel 8-hydroxyquinoline ligand **II** with 2-(pyridine-4-yl)vinyl substituent at position 2 of the quinoline ring was prepared via condensation of 2-methylquinolines **Ia–Ic** with 4-pyridinecarboxaldehyde in acetic acid anhydride. Arylsulfonyloxyquinoline **III** was prepared via reaction of styrylquinoline **IIa** with *p*-toluenesulfonyl chloride in the presence of trimethylamine as base (Scheme 1).

Structures of the prepared compounds **IIa–IIc**, **III** were elucidated taking into account the elemental analysis as well as IR, UV, ^{1}H, and ^{13}C NMR spectroscopy data. Furthermore, luminescent properties of the products were investigated.

^{1}H NMR spectra of styrylquinlolines **IIa–IIc**, **III** contained the vinyl protons signals at 7.23–7.60 and 7.43–7.70 ppm with spin-spin coupling constant of 16.0–17.5 Hz, indicating their *trans*-configuration and coinciding with the earlier reported data [13]. Electronic absorption spectra of the compounds contained long-wave bands maximums due to the π–π* transition at 323–375 nm; a small red shift (by 4–7 nm) of the

Scheme 1.



Ia–Ic **IIa–IIc** **III**

R = H (**a**), Me (**b**), CH_2Ph (**c**).

most long-wavelength absorption band of compounds **IIa**–**IIc** was observed in the more polar solvents. In the case of tosyloxyquinoline **III**, the opposite trend was found (see table).

2-[2-(Pyridine-4-yl)vinyl]quinoline-8-ol **IIa** showed blue-green luminescence (λ_{max} = 438–512 nm) with fairly low quantum yield (φ = 0.001–0.012) due to the ESIPT process operative [6–8]. The luminescence of its methyl (**IIb**) and benzyl (**IIc**) derivatives was more efficient since the ESIPT process was restricted; the emission maximum was shifted towards shorter wavelength (λ_{max} = 434–481 nm, φ = 0.16–0.41). However, quantum yield of luminescence of tosyloxyquinoline **III** was low as well (λ_{max} = 398–546 nm, φ = 0.001–0.003), even though the ESIPT process was not favorable. That could be due to the intercombination singlet-triplet conversion between the $\pi\pi^*$ and $n\pi^*$ levels of non-conjugated quinoline and tosyl fragments.

Absorption and fluorescent (λ_{ex} 350 nm) spectral properties of compounds (**IIa**–**IIc** and **III**)

Comp. no.	λ_{max}, nm ($\varepsilon \times 10^{-4}$, L mol^{-1} cm^{-1})			λ_{max}^{fl}, nm (φ)		
	toluene	acetonitrile	DMSO	toluene	acetonitrile	DMSO
IIa	368 (0.355)	370 (0.450)	375 (0.412)	438 (0.002)	472 (0.006)	510 (0.012)
	350 (0.727)	351 (1.30)	360 (1.20)	512 (0.001)		
	341 (1.51)	338 (1.85)	342 (1.63)			
	334 (1.36)	327 (1.56)	332 (1.39)			
IIb	365 (0.756)	367 (0.477)	371 (0.497)	435 (0.22)	469 (0.28)	481 (0.41)
	349 (1.62)	349 (1.17)	355 (1.32)			
	338 (2.38)	337 (2.35)	340 (2.26)			
	330 (2.21)	325 (2.20)	330 (2.08)			
IIc	360 (0.787)	363 (0.542)	364 (0.790)	434 (0.16)	469 (0.26)	476 (0.27)
	348 (1.66)	349 (1.37)	350 (1.41)			
	340 (2.58)	336 (2.40)	341 (2.32)			
	333 (2.19)	329 (2.26)	331 (2.17)			
III	359 (1.29)	356 (1.02)	355 (1.12)	399 (0.002)	398 (0.001)	417 (0.003)
	351 (1.54)	347 (1.45)	346 (1.78)	414 (0.002)	413 (0.001)	436 (0.003)
	342 (2.25)	338 (2.02)	342 (2.41)			
	330 (2.11)	323 (1.94)	327 (2.25)			

In summary, novel 8-hydroxyquinoline ligand with 2-(pyridine-4-yl)vinyl substituent at position 2 of the quinoline ring and its efficiently light-emitting methyl and benzyl derivatives were prepared; those compounds can be potentially used as highly demanded organic blue luminophors.

EXPERIMENTAL

IR spectra of thin films were recorded with a Varian Excalibur 3100 FT-IR spectrometer. ^{1}H (250.13 MHz) and ^{13}C (62.90 MHz) NMR spectra were registered with a Bruker DPX-250 instrument. Absorption and fluorescence spectra were measured with a Cary Scan 100 and a Cary Eclipse spectrophotometers, respectively. Fluorescence quantum yield was determined as referenced to that of anthracene solution in acetonitrile [14].

2-[(*E*)-2-(Pyridin-4-yl)vinyl]quinolin-8-ol (IIa). A mixture of 0.32 g (0.002 mol) of 8-hydroxy-2-methylquinoline **Ia** and 0.21 g (0.002 mol) of 4-pyridinecarboxaldehyde in 15 mL of freshly distilled acetic anhydride was refluxed during 15 h. Acetic anhydride was distilled off in vacuum, the residue was treated with 3 mL of conc. hydrochloric acid, and the mixture was refluxed during 0.4 h. The mixture was cooled to room temperature and neutralized with saturated solution of sodium bicarbonate to neutral pH. The precipitated solid was filtered off and purified via column chromatography on silica gel 60 μm eluting with CH_2Cl_2 and collecting the fraction with R_f 0.6. After distilling off the solvent, the product was recrystallized from 2-propanol (2 × 15 mL). Yield 0.31 g (62%), pale yellow crystals, mp 162–163°C. IR spectrum, ν, cm^{-1}: 708, 770, 838, 960 (*trans*-CH=CH), 1137, 1156, 1178, 1187, 1231 (C–OH), 1270, 1422, 1434, 1507, 1571, 1599, 1608, 3317 (O–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.17 d (1H, H^7, *J* 7.5 Hz), 7.28 d (1H, H^5, *J* 8.1 Hz), 7.42 d (2H, H$^{3',5'}$, *J* 5.1 Hz), 7.44 d.d (1H, H^6, J_1 7.5, J_2 8.1 Hz), 7.46 d (1H, CH=, *J* 16.3 Hz), 7.59 d (1H, CH=, *J* 16.3 Hz), 7.61 d (1H, H^3, *J* 8.1 Hz), 8.13 d (1H, H^4, *J* 8.1 Hz), 8.27 s (1H, OH), 8.62 d (2H, H$^{2',6'}$, *J* 5.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 110.90 (C^7), 118.15 (C^5), 120.97 (C^3), 121.73 (2C, C$^{3',5'}$), 128.26 (C^{10}), 128.41 (CH=), 131.79 (C^6), 132.81 (CH=), 137.14 (C^4), 138.49 (C^9), 144.05 (C$^{4'}$), 150.80 (2C, C$^{2',6'}$), 152.64 (C^2), 152.74 (C^8). Found, %: C 77.62; H 4.50; N 11.03. $C_{16}H_{12}N_2O$. Calculated, %: C 77.40; H 4.87; N 11.28.

8-Methoxy-2-[(*E*)-2-(pyridin-4-yl)vinyl]quinoline (IIb) was prepared similarly from 8-methoxy-2-methylquinoline **Ib** and 4-pyridinecarboxaldehyde. The product was purified via column chromatography on silica gel 60 μm eluting with $CHCl_3$ and collecting the fraction with R_f 0.5. After distilling off the solvent, the product was recrystallized from 2-propanol (2 × 8 mL). Yield 0.34 g (65%), pale yellow crystals, mp 81–82°C. IR spectrum, ν, cm^{-1}: 754, 831, 867, 970 (*trans*-CH=CH), 1024, 1110, 1175, 1217, 1261, 1330, 1378, 1415, 1429, 1462, 1506, 1558, 1599, 1612. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.86 s (3H, CH_3), 6.80 d (1H, H^7, *J* 8.0 Hz), 7.10 d (1H, H^5, *J* 8.0 Hz), 7.18 d (2H, H$^{3',5'}$, *J* 4.7 Hz), 7.19 d (1H, H^6, *J* 8.0 Hz), 7.21 d (1H, H^4, *J* 8.7 Hz), 7.23 d (1H, CH=, *J* 16.0 Hz), 7.24 d (1H, H^3, *J* 8.7 Hz), 7.43 d (1H, CH=, *J* 16.0 Hz), 8.37 d (2H, H$^{2',6'}$, *J* 4.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 55.77 (CH_3), 108.48 (C^7), 119.73 (C^3), 119.75 (C^5), 121.58 (2C, C$^{3',5'}$), 127.32 (C^3), 128.92 (C^{10}), 131.79 (C^6), 132.81 (CH=), 134.14 (CH=), 136.76 (C^4), 140.28 (C^2), 144.13 (C$^{4'}$), 150.47 (2C, C$^{2',6'}$), 153.99 (C^9), 155.52 (C^8). Found, %: C 77.82; H 5.50; N 10.43. $C_{17}H_{14}N_2O$. Calculated, %: C 77.84; H 5.38; N 10.68.

8-(Benzyloxy)-2-[(*E*)-2-(pyridin-4-yl)vinyl]quinoline (IIc) was prepared similarly from 8-benzyloxy-2-methylquinoline **Ic** and 4-pyridinecarboxaldehyde. The product was purified via column chromatography on silica gel 60 μm eluting with a 1 : 1 ethyl acetate–hexane mixture and collecting the fraction with R_f 0.35. After distilling off the solvent, compound **IIc** was recrystallized from 2-propanol (2 × 10 mL). Yield 0.32 g, colorless crystals, mp 124–125°C. IR spectrum, ν, cm^{-1}: 768, 961 (*trans*-CH=CH), 1098, 1197, 1258, 1324, 1348, 1396, 1422, 1437, 1456, 1464, 1520, 1568, 1606, 1618. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.46 s (2H, CH_2), 7.06 d (1H, H$^{5''}$, *J* 5.2 Hz), 7.34 d.d (2H, H$^{3'',5''}$, J_1 7.4, J_2 7.7 Hz), 7.35 d (1H, CH=, *J* 17.5 Hz), 7.36 d (1H, H^3, *J* 8.6 Hz), 7.37 d (1H, H^5, *J* 8.0 Hz), 7.45 d (2H, H$^{3',5'}$, *J* 5.8 Hz), 7.52 d (1H, H^6, *J* 8.0 Hz), 7.55 d (2H, H$^{2'',6''}$, *J* 7.7 Hz), 7.60 d (1H, CH=, *J* 17.5 Hz), 7.70 d (1H, H^7, *J* 8.0 Hz), 8.12 d (1H, H^4, *J* 8.6 Hz), 8.61 d (2H, H$^{2',6'}$, *J* 5.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 71.02 (CH_2), 100.97 (C^7), 119.87 (C^5), 121.35 (C^3), 126.87 (2C, C$^{2'',6''}$), 127.01 (2C, C$^{3',5'}$), 127.78 (C^6), 127.79 (C$^{4''}$), 128.56 (2C, C$^{3'',5''}$), 128.86 (C^{10}), 131.02 (CH=), 134.03 (CH=), 134.45 (C^8), 136.50 (C$^{1''}$), 137.03 (C^4), 143.12 (C^9), 147.27 (C$^{4'}$), 150.80 (2C, C$^{2',6'}$), 153.81 (C^2). Found, %: C 81.72; H 5.23; N 8.31. $C_{23}H_{18}N_2O$. Calculated, %: C 81.63; H 5.36; N 8.28.

8-(4-Methylphenylsulfonyloxy)-2-[(*E*)-2-(pyridin-4-yl)vinyl]quinoline (III). 0.21 g (0.0011 mol) of *p*-toluenesulfonyl chloride was added at room temperature upon stirring to a mixture of 0.25 g (0.001 mol) of 2-[(*E*)-2-(pyridin-4-yl)ethenyl]quinolin-8-ol and 1 mL of Et_3N in 10 mL of anhydrous benzene. The reaction mixture was incubated during 3 days at room temperature, then refluxed during 2 h, and cooled down to ambient. After filtering off $Et_3N{\cdot}HCl$, the filtrate was evaporated, and the residue was purified on a chromatographic column with Al_2O_3 eluting with chloroform and collecting the fraction with R_f 0.4. After distilling off the solvent, compound **III** was recrystallized from 2-propanol (2 × 12 mL). Yield 0.31 g (77%), colorless crystals, mp 129–130°C. IR spectrum, ν, cm^{-1}: 784, 835, 972 (*trans*-CH=CH), 1042, 1175, 1190 (SO_2), 1217, 1325, 1356 (SO_2), 1433, 1458, 1502, 1551, 1558, 1595. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.25 s (3H, CH_3), 7.18 d (2H, $H^{3'',5''}$, *J* 8.4 Hz), 7.25 d (1H, CH=, *J* 16.1 Hz), 7.41 d (2H, $H^{3',5'}$, *J* 6.0 Hz), 7.46 d (1H, CH=, *J* 16.1 Hz), 7.47 d.d (1H, H^6, J_1 1.3, J_2 8.0 Hz), 7.54 d (1H, H^3, *J* 8.6 Hz), 7.63 d.d (1H, H^7, J_1 1.3, J_2 8.0 Hz), 7.71 d.d (1H, H^5, J_1 1.3, J_2 8.0 Hz), 7.82 d (2H, $H^{2'',6''}$, *J* 8.4 Hz), 8.10 d (1H, H^4, *J* 8.6 Hz), 8.65 d (2H, $H^{2',6'}$, *J* 6.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.56 (CH_3), 120.74 (C^3), 121.34 (2C, $C^{3',5'}$), 123.64 (C^7), 126.17 (C^6), 126.68 (C^5), 128.72 (2C, $C^{2'',6''}$), 128.91 (C^{10}), 129.31 (2C, $C^{3'',5''}$), 132.21 (CH=), 132.39 (CH=), 133.85 ($C^{1''}$), 136.39 (C^4), 141.48 (C^9), 143.65 (C^8), 144.89 ($C^{4'}$), 145.71 ($C^{4''}$), 150.46 (2C, $C^{2',6'}$), 154.74 (C^2). Found, %: C 68.75; H 4.42; N 6.91. $C_{23}H_{18}N_2O_3S$. Calculated, %: C 68.64; H 4.51; N 6.96.

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Education and Science of Russian Federation in the frame of Governmental contract no. 4.129.2014/K.

REFERENCES

1. Jiang, P., and Guo, Z., *Coord. Chem. Rev*., 2004, vol. 248, p. 205. DOI: 10.1016/j.cct.2003.10.013.
2. Valeur, B., and Leray, I., *Coord. Chem. Rev*., 2000, vol. 205, p. 3. DOI: 10.1016/S0010-8545(00)00246-0.
3. Zhang, H., Wang, Q.-L., and Jiang, Y.-B., *Tetrahedron Lett*., 2007, vol. 48, p. 3959. DOI: 10.1016/j.tetlet.2007.04.045.
4. Shults, M.D., Pearce, D.A., and Imperiali, B., *J. Am. Chem. Soc*., 2003, vol. 125, p. 10591. DOI: 10.1021/ja0355980.
5. Mikhailov, I.E., Dushenko, G.A., Starikov, D.A., Mikhailova, O.I., and Minkin, V.I., *Vestn. YuNTs*, 2010, vol. 6, no. 4, p. 32.
6. Bardez, E., Devol, I., Larrey, B., and Valeur, B., *J. Phys. Chem. (B)*, 1997, vol. 101, no. 39, p. 7786. DOI: 10.1021/jp971293u.
7. Serdyuk, O.V., Evseenko, I.V., Dushenko, G.A., Revinskii, Yu.V., and Mikhailov, I.E., *Russ. J. Org. Chem*., 2012, vol. 48, no. 1, p. 78. DOI: 10.1134/S1070428012010113.
8. Beldovskaya, A.D., Dushenko, G.A., Vikrishchuk, N.I., Popov, L.D., Revinskii, Yu.V., and Mikhailov, I.E., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 11, p. 2075. DOI: 10.1134/S1070363213110200.
9. Beldovskaya, A.D., Dushenko, G.A., Vikrishchuk, N.I., Popov, L.D., Revinskii, Yu.V., Mikhailov, I.E., and Minkin, V.I., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 1, p. 171. DOI: 10.1134/S1070363214010290.
10. Beldovskaya, A.D., Dushenko, G.A., Vikrishchuk, N.I., Popov, L.D., Revinskii, Yu.V., Mikhailov, I.E., and Minkin, V.I., *Russ. J. Org. Chem*., 2013, vol. 49, no. 12, p. 1861. DOI: 10.1134/S1070428013120312.
11. Barberis, V.P., and Mikroyannidis, J.A., *Synth. Met*., 2006, vol. 156, p. 865. DOI: 10.1016/j.synthmet.2006.05.007.
12. Mikhailov, I.E., Kolodina, A.A., Dushenko, G.A., Artyushkina, Yu.M., Tkachev, V.V., Aldoshin, S.M., Sayapin, Yu.A., and Minkin, V.I., *Chem. Heterocycl. Compd*., 2014, vol. 50, no. 6, p. 828. DOI: 10.1007/s10593-014-1537-9.
13. Nosova, E.V., Lipunova, G.N., Stupina, T.V., Slepukhin, P.A., Valova, M.S., and Charushin, V.N., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 9, p. 1771. DOI: 10.1134/S1070363214090229.
14. Dushenko, G.A., Vikrishchuk, A.D., Mikhailov, I.E., and Vikrishchuk, N.I., *Vestn. YuNTs*, 2013, vol. 9, no. 1, p. 37.