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Short communication

Synthesis and fluorescent properties of 2-styryl-6,7-difluoro-8-hydroxyquinoline and its Zn(II) complex

Emiliya V. Nosova [a,*], Tatyana V. Stupina [a], Galina N. Lipunova [b], Valery N. Charushin [a,b]

[a] Department of Organic Chemistry, Chemical Technology Institute, Urals Federal University, 19 Mira Str., 620002 Ekaterinburg, Russia
[b] I. Postovsky Institute of Organic Synthesis, Ural Division of the Russian Academy of Sciences, 22 S. Kovalevskoy Str., 620219 Ekaterinburg, Russia

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ABSTRACT

A synthetic approach to 2-methyl-6,7-difluoro-8-hydroxyquinoline, a key intermediate, has been developed. 6,7-Difluoro derivative of 2-styryl substituted 8-hydroxyquinoline and its Zn(II) complex have been obtained. Effects of fluorine atoms in the benzene ring on photophysical properties of 2-styryl-8-hydroxyquinolines and their Zn(II) complexes have been studied.

1. Introduction

8-Hydroxyquinoline and its numerous derivatives and metal chelates have been attracting attention of researchers for two decades, since the first data on the aluminum complex of 8-hydroxyquinoline exhibiting thermal stability, high efficiency of green luminescence, and rather good electronic mobility have been published [1]. On the other hand, there are a limited number of publications in which influence of fluorine atoms in various positions of the quinoline system on luminescence characteristics of aluminum complexes of 8-hydroxyquinoline have been described [2]. Due to specific properties of fluorine atoms metal complexes of fluorinated 8-hydroxyquinolines proved to have an enhanced electronic mobility, a low temperature of sublimation, a good stability in air, and a wide energetic gap. It has been shown [2] that incorporation of a fluorine atom at the 5-position of 8-hydroxyquinoline leads to a red shift of the luminescence maximum (λ_{max} = 547 nm, for nonfluorinated analog 515 nm) with a considerable decrease in both intensity (approximately 20 times) and the quantum yield. At the same time, the aluminum complex of 6-fluoro-8-oxyquinolate demonstrates a blue shift (λ_{max} = 495 nm) with a significant enhancement of the luminescence intensity and 2.6-fold increase in quantum yield. Fluorination of the 7-position of 8-hydroxyquinoline has practically no effect on the luminescent properties. Also it has been reported that in case of metal complexes of difluoro substituted 8-hydroxyquinolines contacts of an electrode with organic materials are facilitated [3].

2-Styryl derivatives of fluorinated 8-hydroxyquinolines have not so far been described. It should be noted that quinoline ligands are often modified by means of extension of the conjugated chain by a substituent, for example the styryl fragment, attached to 2- or 4-positions of the pyridine ring [4]. Complexes of 2-styryl-8-hydroxyquinolines have been shown to possess improved properties relative to the corresponding complexes 8-hydroxyquinoline. They are well soluble in common organic solvents, thermally stable and more suitable for preparation of films. Solutions of these complexes in THF exhibit blue-green luminescence with a maximum in the range of 513–576 nm, and λ^{fl}_{max} for zinc compounds being more red-shifted. Nowadays a great attention is given to elucidation of photophysical properties of complexes of styryl substituted 8-hydroxyquinolines with zinc and aluminum. In this communication we wish to report on the synthesis of 6,7-difluoro-2-styryl-8-hydroxyquinoline and its Zn(II) complex, and their characteristics and photophysical properties in comparison with those of non-fluorinated analogs have first been discussed.

2. Results and discussion

We have first obtained 2-methyl-6,7-difluoro-8-oxyquinoline **3** from 2,3-difluoro-6-nitrophenol **1** (Scheme 1). The intermediate **3**

* Corresponding author. Tel.: +7 343 3754501.
E-mail addresses: emily74@rambler.ru, emilia.nosova@yandex.ru (E.V. Nosova), lipunova@ios.uran.ru (G.N. Lipunova).

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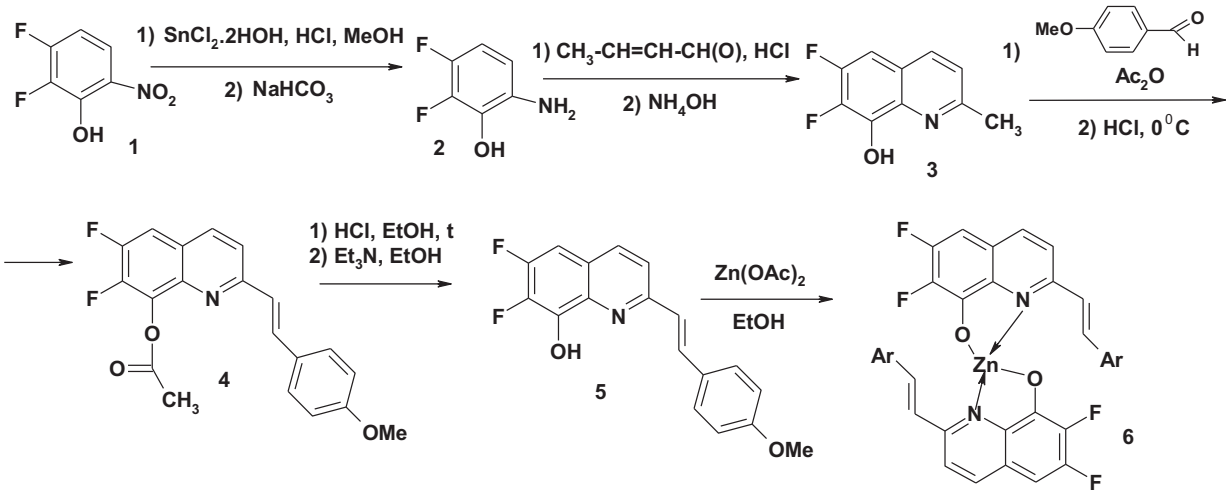


Scheme 1. Compound **6**: Ar = 4-methoxyphenyl.

was synthesized from the corresponding nitrophenol **1** by reduction with $SnCl_2$ followed by the Skraup quinoline synthesis with crotonic aldehyde in the presence of HCl (Scheme 1). A similar approach has been used to reduce 2-nitro-4-bromphenol [5], earlier aminophenol **2** was synthesized by reduction of compound **1** with palladium monocarbide [6], and appropriate condensation conditions have been reported for the synthesis of 2-methyl-6,7-difluoroquinoline [7].

The acetoxy derivative **4** was obtained from quinoline **3**. In the NMR ^1H spectrum of compound **4** two characteristic doublets of CH=CH protons (at 7.24 and 7.72 ppm with ^3J 16.3 Hz) were observed, thus indicating that the molecule has the *trans*-configuration of the alkenyl fragment. Perkin condensation of 2-methyl-8-oxyquinolines was reported [8]. Hydrolysis of acetoxygroup of **4** was carried out by the heating with hydrochloric acid in ethanol, for transformation of hydrochloride of 2-styryl-8-oxyderivative into free ligand **5** reaction mixture was treated with triethylamine (Scheme 1). The structural evidence for compound **5** has been confirmed by the ^1H, ^{13}C NMR and mass spectra.

Complex **6** was obtained by heating of hydroxystyrylquinoline **5** with zink(II) acetate in the molar ratio 2:1 in ethanol (Scheme 1). The ^1H NMR spectra of complex **6** shows no OH signals; the signals of H^4 and H^3 protons of the pyridine ring are shifted downfield compared to those in ligand **5**, while the signal of H^5 proton of the benzene ring is shifted upfield compared to the corresponding signal of the same ligand. The signal of F^7 of 8-hydroxyderivative **5** in ^{19}F NMR spectra is shifted upfield compared to these in 8-acetoxyquinoline **4** (−147.74 ppm for **4** and −159.05 ppm for **5**), the signal of F^7 fluorine of complex **6** is shifted also upfield compared to these in ligand **5** (−159.05 ppm for **5** and −163.33 ppm for **6**).

In the IR spectra of complex **6** there are no bands at 3340–3375 cm^{-1} (valent fluctuations of O–H) and 1330–1335 cm^{-1} (deformational fluctuations of O–H), while the band at 1229–1237 cm^{-1} is weak (valent fluctuations C–O) because of coordination of the oxygen atom with a metal ion. In the UV–vis absorption spectra of complex **6** batochromic shifts for the long-wave band of approximately 70 nm is observed in comparison with these of the corresponding ligand (Table 1).

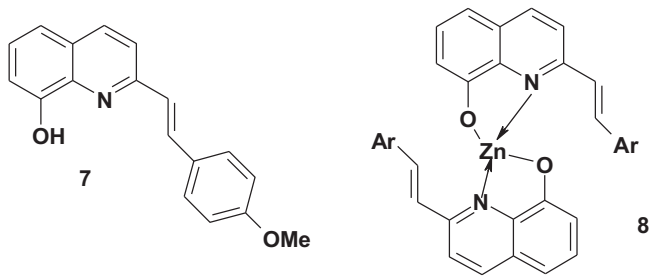
Absorption and emission spectra of compounds **5** and **6** were recorded in MeCN solutions at room temperature and compared with spectra of non-fluorinated analogs **7** and **8** (Scheme 2 and Table 1).

Difluoro derivative **6** showed blue shift of the emission peak in comparison with the chelate **8** which does not bearing fluorine atoms in a benzene ring. Difluoro derivative of 8-hydroxy-2-styrylquinoline showed red shift of the emission peak (compounds **5** and **7**) (Table 1). The analysis of literary data [2] allows to assume that observed shifts of the emission peaks are due to the fluorine atom at the 6 position.

Table 1
The absorbtion and fluorescence maxima for compounds **5–8** in acetonitrile at 293 K.

Compound	λa (nm)	λf (nm)[a]	Stokes shift (nm)
5	352	455	103
6	420	559	139
7	320	427	107
8	435	599	164

[a] Excitement in the field of an absorption maximum.



Scheme 2. Non-fluorinated analogs of **5** and **6**. Compound **8**: Ar = 4-methoxyphenyl.

3. Conclusion

In conclusion it is worth noting incorporation of fluorine atoms in styryl substituted quinolines appears to be a good approach to tune their photophysical properties. Indeed, novel fluorinated quinolines **3** and **5** proved to be attractive compounds for preparing of other metal complexes, for example Al(III).

4. Experimental

4.1. General

Difluoro-6-nitrophenol **1** was obtained from 2,3,4-trifluoronitrobenzene according to the method described in the literature [9] and compounds **7** and **8** were synthesized as described [4a].

NMR, MS and analytical data for compounds obtained are presented in Supporting information.

4.2. Synthesis of 2-amino-5,6-difluorophenol (2)

To a solution of $SnCl_2 \cdot 2H_2O$ (32.1 g, 142.8 mmol) in methanol (100 mL) a concentrated hydrochloric acid (70 mL) and 2,3-difluoro-6-nitrophenol **1** (5.0 g, 28.5 mmol) at 0 °C were added. The reaction mixture was stirred at room temperature for 48 h, the solution has decolorated. Solution was neutralized with water $NaHCO_3$ to pH 7, the formed colorless solid was filtered, dried at room temperature and extracted with ethyl acetate for several times. Water filtrate was extracted with ethyl acetate, combined organic lays were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Yield of 2-amino-5,6-difluorophenol is 3.5 g (84%), mp. 128–130 °C is in full agreement with the literature [6].

4.3. Synthesis of 2-methyl-5,6-difluoro-8-hydroxyquinoline (3)

To 2-amino-5,6-difluorophenol **2** (2 g, 13.8 mmol) 6 N hydrochloric acid (10 mL) was added, the mixture was heated to 100 °C, then crotonic aldehyde (1.2 mL, 14.3 mmol) was added slowly. The mixture was refluxed for 16 h, after cooling NH_4OH was added under stirring to pH 8. Then ethyl acetate (50 mL) was added, and the reaction mixture was stirred during 30 min, the formed colorless solid was filtered. Filtrate was extracted with ethyl acetate, organic solution was concentrated in vacuo, and residue was recrystallized from hexane–ethanol (1:1). Yield of 2-methyl-5,6-difluoro-8-hydroxyquinoline is 1.36 g (51%), mp. 102–104 °C.

4.4. Synthesis of (E)-2-[2-(4-methoxyphenyl)vinyl]-6,7-difluoro-8-acetoxyquinoline (4)

To a solution of quinoline **3** (0.4 g, 2.05 mmol) in acetic anhydride (10 mL) *p*-methoxybenzaldehyde (0.5 mL, 2.9 mmol) was added. The mixture was refluxed during 20 h, and then it was poured into ice (50 mL) and under stirring 5 drops of hydrochloric acid was added. The formed red-brown solid was filtered and recrystallized from ethanol. Yield of (*E*)-2-[2-(4-methoxyphenyl)-vinyl]-6,7-difluoro-8-acetoxyquinoline is 0.41 g (56%), mp. 118–120 °C.

4.5. Synthesis of (E)-2-[2-(4-methoxyphenyl)vinyl]-6,7-difluoro-8-hydroxyquinoline (5)

Acetoxy derivative **4** (0.4 g, 1.13 mmol) was dissolved in ethanol (15 mL) and hydrochloric acid (1.5 mL) was added. The mixture was refluxed for 1 h, cooled to room temperature and concentrated in vacuo, the residue obtained was washed with water (15 mL). The solid obtained was dissolved in ethanol (12 mL), triethylamine (2.5 mL) was added, and the mixture was stirring at room temperature during 3 h, and then concentrated in vacuo. The residue obtained was recrystallized from hexane:ethanol (1:1). Yield of (*E*)-2-[2-(4-methoxyphenyl)vinyl]-6,7-difluoro-8-hydroxyquinoline is 0.16 g (46%), mp. 130–132 °C.

4.6. Synthesis of (E)-2-[2-(4-methoxyphenyl)vinyl]-6,7-difluoro-8-hydroxyquinolinate Zn(II) (6)

To a solution of quinoline **5** (0.125 g, 0.4 mmol) in ethanol (20 mL) zink(II) acetate (0.04 g, 0.2 mmol) was added, the reaction mixture was refluxed for 6 h, and the formed solid was filtered off. Yield of Zn(II) complex **6** is 0.062 g (45%), mp. >300 °C.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2013.03.005.

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