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Structure and Photoluminescent Properties of 2-Methyl-6,7-difluoro-8-hydroxyquinoline

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Abstract—The effect of fluorine atoms in the benzene ring on the photophysical properties of 2-methyl-6,7-difluoro-8-hydroxyquinoline is studied.

Keywords: 2-methyl-6,7-difluoro-8-hydroxyquinoline, absorption spectrum, excitation spectrum, fluorescence, frontier orbitals

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Intra and intermolecular proton transfer is one of the most fundamental and important processes in chemistry and biology. Depending on specific features of the system, various types of proton transfer occur in the ground or excited state. Most interesting from the theoretical and experimental point of view is the Excited State Intramolecular Proton Transfer (ESIPT) [1, 2]. The photoinduced ESIPT is normally observed in organic compounds having both a protic acidic group and a basic center with an intramolecular hydrogen bond [3].

8-Hydroxyquinoline containing the phenol hydroxyl and the pyridine nitrogen atom, as well as its numerous derivatives and metal chelates attracted attention of researchers since the first data on the aluminum complex of 8-hydroxyquinoline (AlQ_3) demonstrating intense green fluorescence, thermal stability, and good electronic mobility have been published [4–10]. Recently, computational methods were applied to investigate aromatic properties of 8-hydroxyquinoline in its different forms (anionic, neutral, zwitter-ionic, and cationic), as well as of chelates with magnesium and aluminum [11]. Principal data on photophysical properties of 8-hydroxyquinoline (8-HQ) as well as 5-, 6-, and 7-hydroxyquinolines in various conditions, in particular, in aqueous solutions, were published before 1980. It was shown that these derivatives similarly exhibited an intense fluorescence in concentrated acids, which was quenched by small amount of water [12]. Goldman and Wehry [12] came to the conclusion that the fluorescence of zwitter-ionic forms of 5- and 8-hydroxyquinolines in aqueous solutions was absent. Later on, the processes in the excited state of 6-hydroxyquinoline were studied in acidic, basic, and neutral media [13]. In the spectrum of fluorescence of 6-hydroxyquinoline in the neutral form not only the band of emission of the N* form appears (λ_{max} = 380 nm), but also the band of the T* form (λ_{max} = 580 nm). It was concluded that photophysical behavior of 6-hydroxyquinoline and especially its very low quantum yield (5×10^{-3}) can be explained by double proton transfer (deprotonation of OH, protonation of N) combined with the intramolecular electron transfer. Interaction between the two functional groups (OH and N) in the excited state, apparently, results in the enhanced photoacidity and photobasicity of the molecule due to the interaction between the proton and electron transfer. Bardez et al. [13] explained a rather weak emission and suggested the quinoid structure of the photoproduct T* differing from the structure of the zwitter-ionic type, which was suggested by them in previous works. It was shown that the suggested scheme is also true for 5-, 7- and 8-hydroxyquinolines (Scheme 1).

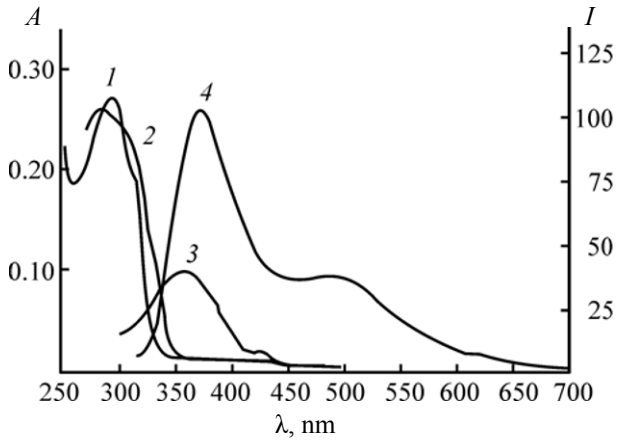


Fig. 1. (*1*) Spectra of absorption, (*2*) excitation at λ_{obs} = 371 nm, (*3*) excitation at λ_{obs} = 488 nm, and (*4*) emission at λ_{ex} = 293 nm of quinoline **I** in acetonitrile at room temperature.

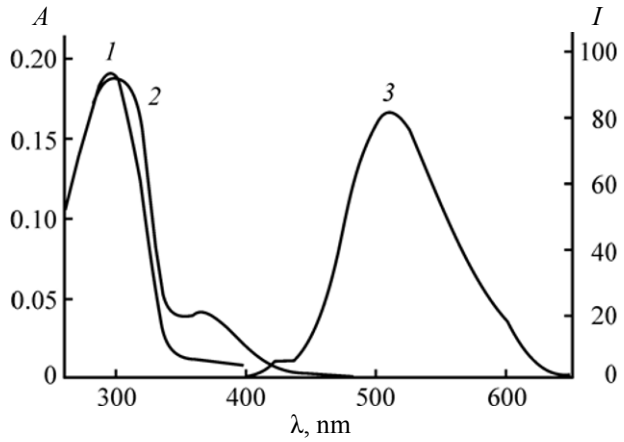
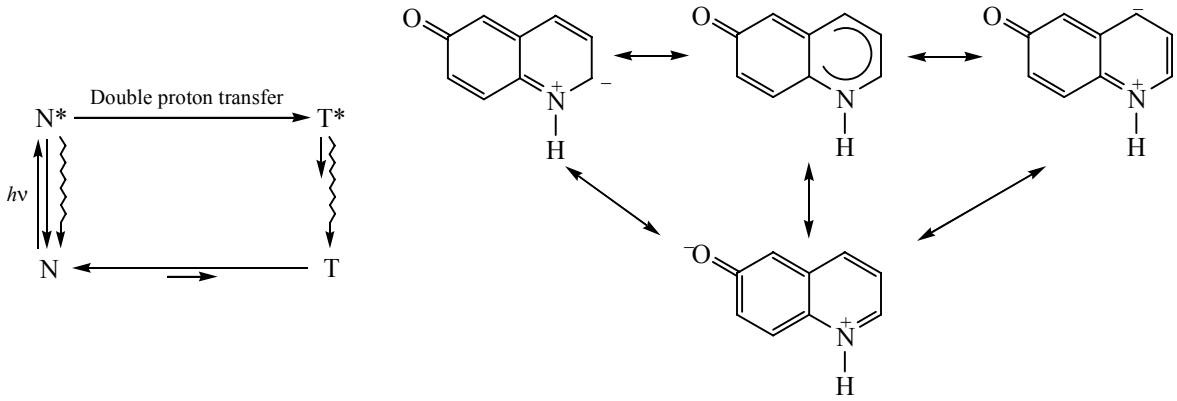


Fig. 2. (*1*) Spectra of absorption, (*2*) excitation at λ_{obs} = 506 nm, and (*3*) emission at λ_{ex} = 296 nm of quinoline **I** in DMSO at room temperature.

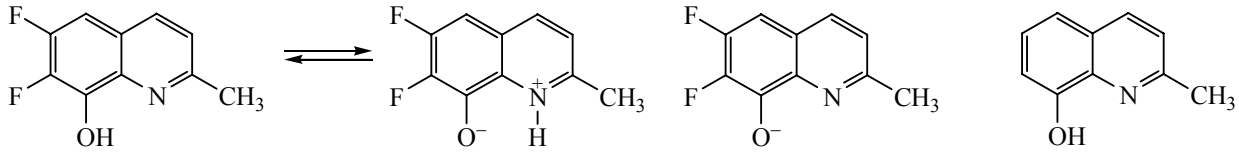
In the present work we report on photoluminescent properties of 2-methyl-6,7-difluoro-8-hydroxyquinoline (**I**) in organic solvents in comparison with the properties of its nonfluorinated analog, 2-methyl-8-hyd-roxyquinoline (**II**) (Scheme 2).

UV spectra of compound **I** in acetonitrile, dimethylsulfoxide, chloroform, and ethanol have absorption bands at λ_{max} = 293, 296, 300, 293 nm, respectively, as well as weak absorption bands at 350–450 nm (Figs. 1–4, Table 1). Compound **I** possesses photoluminescent properties, but the spectral pattern varies depending on the nature of the solvent. In the emission spectrum of compound **I** in acetonitrile (at the excitation in the region of 293 nm) not only a strong band at λ_{max} = 371 nm was registered but also a less intense band at λ_{max} = 488 nm (Fig. 1, curve *4*). In the excitation spectrum at the wavelength of the emission maximum (371 nm) the registered spectrum (Fig. 1, curve *2*) practically coincides with the absorption

Scheme 1.



Scheme 2.



Ia **Ib** **Ic** **II**

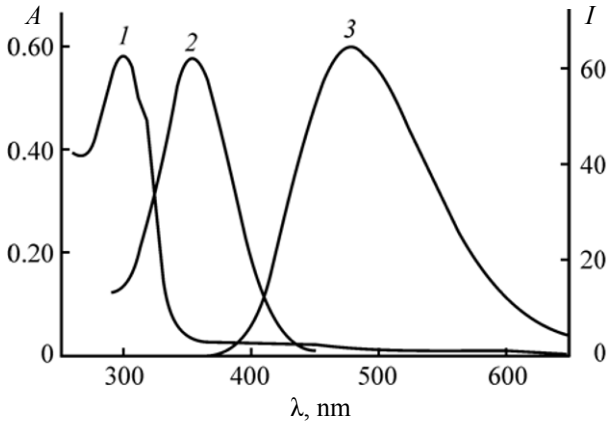


Fig. 3. (*1*) Spectra of absorption, (*2*) excitation at λ_{obs} = 483 nm, and (*3*) emission at λ_{ex} = 300 nm of quinoline **I** in $CHCl_3$ at room temperature.

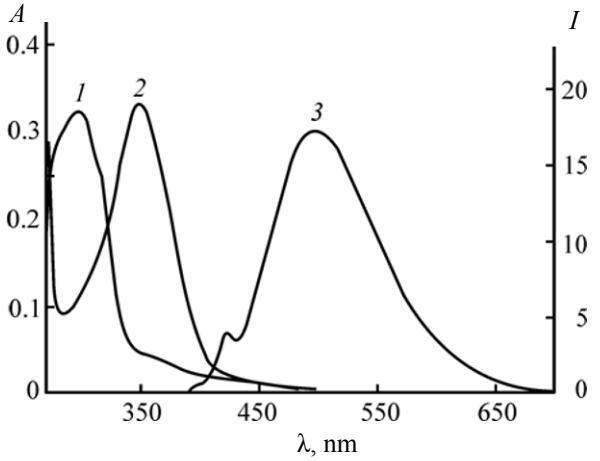


Fig. 4. (*1*) Spectra of absorption, (*2*) excitation at λ_{obs} = 493 nm, and (*3*) emission at λ_{ex} = 350 nm of quinoline **I** in ethanol at room temperature.

spectrum (Fig. 1, curve *1*), and at the wavelength of 488 nm the excitation spectrum is observed with maximum at 362 nm (Fig. 1, curve *3*).

The excitation of the DMSO solution of compound **I** by the light of the wavelength 296 nm gives rise to the appearance of an intense green fluorescence with the maximum at 506 nm (Fig. 2, curve *3*). However, the excitation spectrum is somewhat different from the absorption spectrum: along with the band with λ_{max} = 300 nm a band with λ_{max} = 360 nm is observed (Fig. 2, curve *2*).

The solution of compound **I** in chloroform shows green fluorescence with maximum at 483 nm at the excitation in the range of 300 nm (Fig. 3, curve *3*). When recording the excitation spectrum at the emission wavelength (λ_{max} = 483 nm) the obtained

Table 1. Optical properties of compounds **I, II**

Comp. no.	Solvent	λ_{max}^{abs}, nm (*D*)	λ^{ex}, nm	λ_{max}^{em}, nm	φ	Stokes shift $\Delta\nu_{St}$, cm^{-1}
I	MeCN	236 (2.54), 293 (0.27), 320 (0.17)	281	371	0.0007	7176
			362	488		13638
	$CHCl_3$	300 (0.58)	350	483	0.0001	12629
	DMSO	296 (0.73)	300, 360	506	0.0030	14021
	MeCN + *t*-BuOK	238 (0.58), 261 (0.62), 316 (0.07), 341 (0.07), 384 (0.06)	262, 340, 383	518	0.0815	6737
	EtOH	238 (0.77), 256 (0.27), 293 (0.08)	350	493	0.002	13846
	EtOH + *t*-BuOK	351 (0.07), 256 (0.79)	348	499	0.009	8696
	PMMA	297	Luminescent properties not detected			
II	MeCN	240 (3.17), 302 (0,28)	301	390	0.0015	7472
	DMSO	307 (0,22)	301	409	0.0053 0	8123

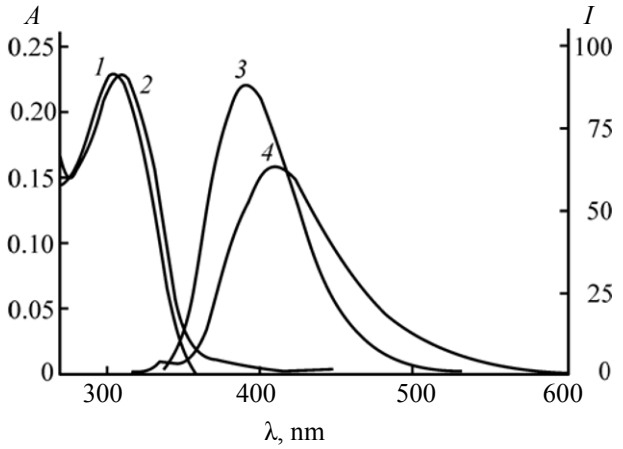


Fig. 5. (*1, 2*) Spectra of absorption, excitation [(*3*) λ_{obs} = 394 nm and (*4*) λ_{obs}= 409 nm], emission [(*3*) λ_{ex} = 312 nm and (*4*) λ_{ex} = 308 nm] of quinoline **II** in (*1, 3*) acetonitrile and (*2, 4*) DMSO at room temperature.

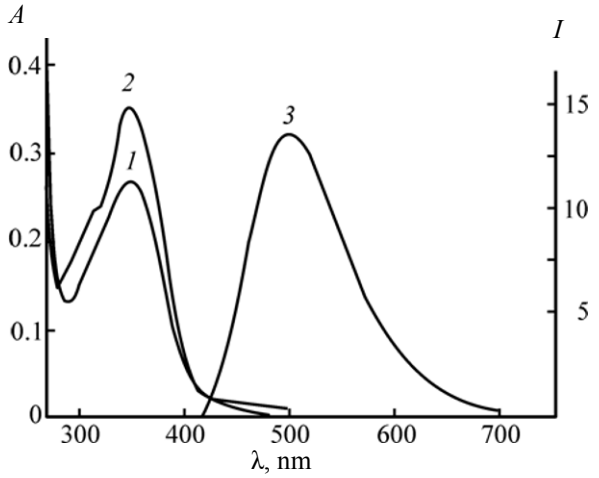


Fig. 6. (*1*) Spectra of absorption, (*2*) excitation at λ_{obs} = 499 nm, (*3*) emission at λ_{ex} = 351 nm of quinoline **I** in ethanol in the presence of *t*-BuOK at room temperature.

spectrum (Fig. 3, curve *2*) was different from the absorption spectrum.

When exciting the ethanol solution of compound **I** by the light with λ = 293 nm a green fluorescence was observed with the maximum at 493 nm (Fig. 4, curve *3*). The excitation spectrum at the wavelength of the emission maximum (λ = 493 nm) (Fig. 4, curve *2*), as in the case of the chloroform solution, differs from the absorption spectrum of (Fig. 4, curve *1*).

2-Methyl-6,7-difluoro-8-hydroxyquinoline (**I**) exists in the hydroxyl form **Ia** and zwitter-ionic form **Ib** due to the presence of both acidic and basic groups. Along with the presence of monomers, the formation of dimers with hydrogen bonds or proton transfer is possible [15].

According to the data of ^{1}H NMR spectroscopy, in CD_3CN, $CDCl_3$ and DMSO-d_6 solutions the zwitter-ionic form **Ib** is present, as proved by the absence of signals of OH protons and the presence of a broadened upfield singlet of NH^+ groups at 4.23 (DMSO-d_6), 5.32 ($CDCl_3$) and 5.43 ppm (CD_3CN).

In the luminescence spectra of solutions of compound **I** in ethanol, DMSO, chloroform, and acetonitrile the emission band at 483–506 nm is present and a large Stokes shift in the fluorescence spectra, as well as a band with λ_{max} = 350–362 nm in the corresponding excitation spectrum (Table 1).

Unlike compound **I**, the nonfluorinated 2-methyl-8-hydroxyquinoline (**II**) shows only one maximum in the emission spectrum with λ_{max} = 390 nm in acetonitrile and with λ_{max} 409 nm in DMSO (Fig. 5). When recording the excitation spectrum at the wavelength of the emission maximum the obtained spectrum coincided with the absorption spectrum (Fig. 5, curves *1, 2*).

In the ^{1}H NMR spectrum of quinoline **II** the signal of the OH proton is observed as a broadened singlet at 8.9 ppm (in DMSO) or at 8.3 ppm (in $CDCl_3$), which is indicative of the presence of the neutral form of quinoline **II** in these solvents.

Comparison of the emission spectra of compound **II** (λ_{em} = 390 nm) with its fluorinated analog **I** (λ_{em} = 371 nm) in acetonitrile shows that introduction of fluorine atoms in the 6 and 7 positions of quinoline causes a blue shift, which is consistent with the literature data [6, 14, 16].

The presence of a longwave band (483–506 nm) in the emission spectrum of compound **I** is apparently due to the effect of fluorine atoms on the electronic structure and prototropic balance.

The acidity of phenol is known to be increased in the excited state [13, 15], which may be due to proton transfer and the process of deprotonation. The data on such processes and appearance of longwave bands in the emission spectra of 4-hydroxystyrylpyridines and diazines are available in the literature [17, 18]. The introduction of fluorine atoms in the 6 and 7 positions of the quinoline molecule increases the acidity of the hydroxyl groups of compound **I**. A similar effect of

other halogens was reported in the literature (for example, the value of pK_a of 2-methyl-8-hydroxyquinoline is equal to 11.63, while that of 5,7-dichloro-8-hydroxyquinoline is 8.90 [19]). It is possible that even in the ground state the anionic form **Ic** exists in the equilibrium with the neutral and zwitter-ionic forms of compound **I**, and the amount of the anionic form increases in the excited state.

In order to detect the anionic form **Ic**, we have recorded the spectra of solutions of quinoline **I** in ethanol and acetonitrile in the presence of *t*-BuOK. In the UV spectra of these solutions the bands with λ_{max} = 351 nm (EtOH, Fig. 6, curve *1*), 340, and 383 nm (MeCN, Fig. 7, curve *1*) are observed. Upon excitation in the range 351 nm (EtOH) or 340 nm (MeCN) an intense green fluorescence with the emission maximum at 499 nm (Fig. 6, curve *3*) or at 518 nm (Fig. 7, curve *3*) was observed. When recording the excitation spectrum at the wavelength of the emission maximum the registered spectra coincided with the absorption spectra (Figs. 6, 7, curves *2*). The excitation spectrum of form **Ic** corresponds to the longwave bands in the excitation spectrum of **I** in solutions in acetonitrile, DMSO, chloroform, and ethanol (Fig. 1, curve *3*; Figs. 2–4, curves *2*).

Note a rather high quantum yield for the anionic form **Ic** in acetonitrile solution (Table 1). The quantum yield of luminescence of compound **II** is almost twice as that of the fluorinated analog **I** and is increased 3–4 times for both compounds in DMSO as compared to acetonitrile solutions (Table 1). Compound **I** does not show photoluminescent properties in polymethylmetacrylate (PMMA) or polycrystalline films (Table 1).

According to calculations performed at the B3LYP/6-31+G(d,p) level using the polarizable continuum model (solvent acetonitrile), the zwitter-ionic NH-form **Ib** is somewhat more stable than the neutral OH-form **Ia**, the difference being 0.61 kcal/mol. The possibility of formation of different forms of compound **I** in acetonitrile was also proved experimentally by the use of electronic spectroscopy method (Table 1). To assign the observed absorption bands to specific electronic transitions we simulated them for all possible forms of compound **I** using the time-dependent DFT method [B3LYP/6-31+G(d,p), PCM (acetonitrile)]. The calculations have shown that the registered absorption peak at 293 nm (D = 0.27) appears due to $S_0 \rightarrow S_5$ transition in the NH-form at λ = 271.82 nm. At the same time, the peak at 320 nm

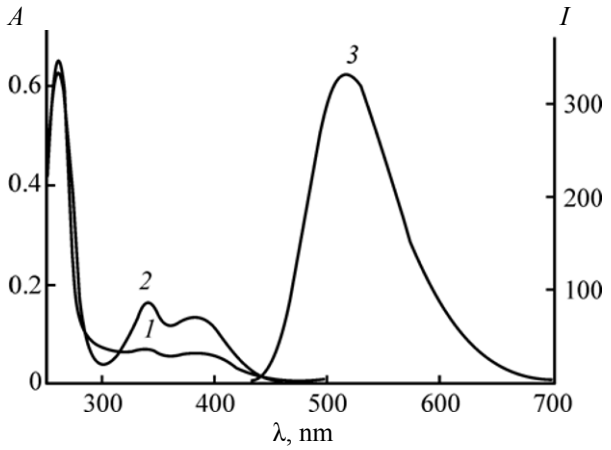


Fig. 7. (*1*) Spectra of absorption, (*2*) excitation at λ_{obs} = 518 nm, (*3*) emission at λ_{ex} = 261 nm of quinoline **I** in acetonitrile in the presence of *t*-BuOK at room temperature.

appears apparently due to $S_0 \rightarrow S_2$ transition in the anion; theoretically, this peak should appear at 316.36 nm. The orbitals corresponding to these transitions (Table 2) are mainly the frontier orbitals.

From the obtained data it can be concluded that quinoline **I** exists mainly in the zwitter-ionic form in DMSO, chloroform, or ethanol solutions. In acetonitrile, the equilibrium is shifted towards the neutral form and a blue fluorescence appears (λ_{max} = 371 nm). Longwave bands in the emission spectra of the solutions of quinoline **I** in DMSO, acetonitrile, chloroform, and ethanol are due to the anionic form, which shows a higher quantum yield. Even small amounts of this form give rise to appearance of the band at 488 nm (MeCN), 483 nm ($CHCl_3$), 493 nm (EtOH), and 506 nm (DMSO) in the emission spectrum. Comparing the behavior of compounds **I** and **II** one can conclude that the introduction of the fluorine atoms in the 6 and 7 positions of 2-methyl-8-hydroxyquinoline strongly affects its fluorescent properties.

Table 2. Energy of frontier orbitals [B3LYP/6-31+G(d,p)]

Comp. no.	E^{HOMO}, eV	E^{LUMO}, eV	ΔE, eV
Ia	–8.37	–1.79	6.58
Ib	–8.40	–2.45	5.95
Ic	–4.81	–1.04	3.77

EXPERIMENTAL

^{1}H NMR spectra were taken on a Bruker DRX-400 spectrometer at working frequency of 400.13 MHz with TMS as an internal reference. ^{19}F NMR spectra were taken on a Bruker Avance 400 spectrometer at working frequency of 376.45 MHz with $CFCl_3$ as an internal reference. Absorption spectra were obtained on a UV-2401PC (Shimadzu, Japan) absorption spectrometer using cells 1 cm thick, concentration 0.0001 mmol/mL (acetonitrile). Emission spectra were registered on a Cary Eclipse (Varian, USA) spectrofluorimeter. Calculations were performed using WestGrid equipment (Canada).

2-Methyl-5,6-difluoro-8-hydroxyquinoline (I) was prepared by the known procedure [11]. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 2.74 s (3H, CH_3), 5.32 br.s (1H, HN^+), 7.04 d.d (1H, H^5, ^3J 10.6, ^4J 7.4 Hz), 7.33 d (1H, H^3, J 8.4 Hz), 7.99 d (1H, H^4, J 8.4 Hz). ^{19}F–{^{1}H} NMR spectrum ($CDCl_3$, δ, ppm): –158.84 d (F^7, J 19.8 Hz), –134.60 d (F^6, J 19.8 Hz). ^{1}H NMR spectrum (CD_3CN, δ, ppm): 2.73 s (3H, CH_3), 5.43 br.s (1H, HN^+), 7.21 d.d (1H, H^5, ^3J 11.0, ^4J 7.8 Hz), 7.44 d (1H, H^3, J 8.5 Hz), 8.13 d (1H, H^4, J 8.5 Hz). ^{19}F–{^{1}H} NMR spectrum (CD_3CN, δ, ppm): –161.76 d (F^7, J 19.1 Hz), –137.77 d (F^6, J 19.1 Hz). ^{1}H NMR spectrum (DMSO-d_6, δ, ppm): 2.71 s (3H, CH_3), 4.23 br.s (1H, HN^+), 7.18 d.d (1H, H^5, ^3J 10.8, ^4J 7.8 Hz), 7.36 d (1H, H^3, J 8.4 Hz), 8.10 d (1H, H^4, J 8.4 Hz). ^{19}F–{^{1}H} NMR spectrum (DMSO-d_6, δ, ppm): –159.11 d (F^7, J 20.6 Hz), –136.25 d (F^6, J 20.6 Hz). Found, %: C, 61.60; H, 3.62; N, 7.18. $C_{10}H_7F_2NO$. Calculated, %: C, 61.54; H, 3.62; N, 7.18.

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