

## 8-Hydroxyquinoline derivatives with 2-pyrazoline fragment in chromophore system as chelating agents for polyvalent metals

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Received December 13, 2007

A group of compounds is described containing two connected structure fragments in molecules, the chelating 8-hydroxyquinoline and fluorescent aryl-2-pyrazoline. Such compounds may be of good prospects in chemical analysis as well as in medical and biological field. The study of absorption and fluorescence spectra of the initial compounds and their complexes with metal ions have shown a high sensitivity of the spectra to complexing process, thus suggesting their potential as chelating agents.

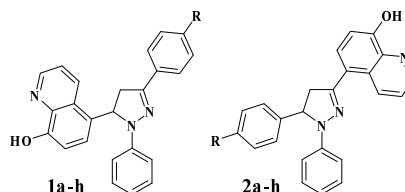
Описана группа соединений, содержащих в молекулах два соединенных структурных фрагмента — хелатообразующий 8-гидроксихинолиновый и флуоресцентный арил-2-пиразолиновый. Такие соединения могут быть перспективными как в химическом анализе, так и в медико-биологических приложениях. Исследование спектров поглощения и флуоресценции исходных соединений и их комплексов с ионами металлов показало высокую чувствительность спектров к процессам комплексообразования, что позволяет предполагать их перспективность в качестве хелаторов.

8-Hydroxyquinoline derivatives are known to be efficient complexing agents of chelating type [1] that provide a high stability of their complexes with metal ions. 8-hydroxyquinoline (HQ) absorbs light in the UV region, that is why the complex formation is not suitable to detect using optical methods. Therefore, it would be of interest to develop novel metal indicating reagents by combining in a single molecule the chelating HQ fragment and diaryl-2-pyrazoline one, the latter being characterized by high fluorescence characteristics [2]. The derivatives of both heterocyclic systems are known to exhibit high physiological activity [1, 3, 4], thus, the novel systems might be of promise both in chemical analysis and in medical and biological fields.

There are only three compounds from the group of interest are mentioned in literature [5]. We have synthesized the compounds **1a-h** and **2a-h** proceeding from 8-hydroxyquinoline analogs of chalcone [6]

using the standard procedures for pyrazolines [7]. The composition and structures of the compounds have been confirmed using elemental analysis, IR,  $^1\text{H}$  NMR, and electron spectroscopy.

The **1a-h** derivatives absorb light from near UV region (370–380 nm), while the **2a-h** series is characterized by a longer-wavelength absorption in visible range (410–420 nm). Worth of attention is a low fluorescence efficiency of both series under study, that is atypical of 2-pyrazolines as a whole. Perhaps such a behavior of the **1a-h** compounds may be caused by a specific in-



R = H (a), CH<sub>3</sub> (b), OCH<sub>3</sub> (c), N(CH<sub>3</sub>)<sub>2</sub> (d), Cl (e), Br (g), NO<sub>2</sub> (h)

tramolecular quenching of fluorescence due to the acceptor in the 5 position of pyrazoline ring [8, 9] or by the possible intramolecular proton transfer in **2a-h** that is often accompanied by nonradiative dissipation of the electron excitation energy [10].

The compounds of both groups have been found to be efficient complexing agents for polyvalent metals. So magnesium and calcium complexes of **1a-h** and **2a-h** were precipitated from ethanol/water medium (where the measurements were carried out) so fastly and completely, that it was impossible to determine their optical characteristics. The chelation of zinc ions was accompanied by a small shift of the absorption and fluorescence spectra that was more pronounced for the **2a-h** compounds.

The complexing properties of the **2a-h** compounds are most pronounced when aluminum ions are complexed. The bathochromic effect amounts 40–45 nm in this case and the bathofluoric one 125 nm (see Fig.), the fluorescence intensity being increased appreciably. These results show a potential for use of similar pyrazoline/hydroxyquinoline systems also in electroluminescence light sources that are under a rather great interest in the last decade [11]. In contrast to the **2** series, pyrazolines **1a-h** do not exhibit any substantial changes in the spectra when aluminum chloride is added. This fact could be connected with the absence of conjugation between the chromophore and complexing fragment in their molecules.

Thus, combination of a fluorophore fragment (1,5-diaryl-2-pyrazoline) with a complexing center (8-hydroxyquinoline) in a single molecule results in formation of efficient sensor systems sensitive to polyvalent metal ions. The detailed quantitative study of the complexing physical chemistry for compounds **1a-h** and **2a-h** will be described later on.

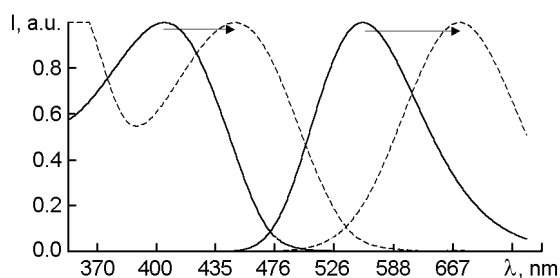


Fig. Normalized absorption and fluorescence spectra of **2g** in ethanol (solid line) and of **2g** in ethanol with  $\text{AlCl}_3$  additive (dashed line).

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## Похідні 8-гідроксихіноліну з фрагментом 2-піразоліну у хромофорній системі як хелатори для іонів полівалентних металів

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Описано групу сполук, що містять у молекулах два суміщених структурних фрагменти — хелатоутворюючий 8-гідроксихіноліновий та флуоресцентний арил-2-піразоліновий. Такі сполуки можуть бути перспективними як у хімічному аналізі, так і у медико-біологічних застосуваннях. Дослідження спектрів поглинання та флуоресценції вихідних сполук та їхніх комплексів з іонами металів показало високу чутливість спектрів до процесів комплексоутворення, що дозволяє припустити їхню перспективність як хелаторів.