

SHORT
COMMUNICATIONS

Crown-Containing Schiff Base Derived from 5-Hydroxy-6-nitro-2,3-tetramethylenebenzo[*b*]furan-4-carbaldehyde*

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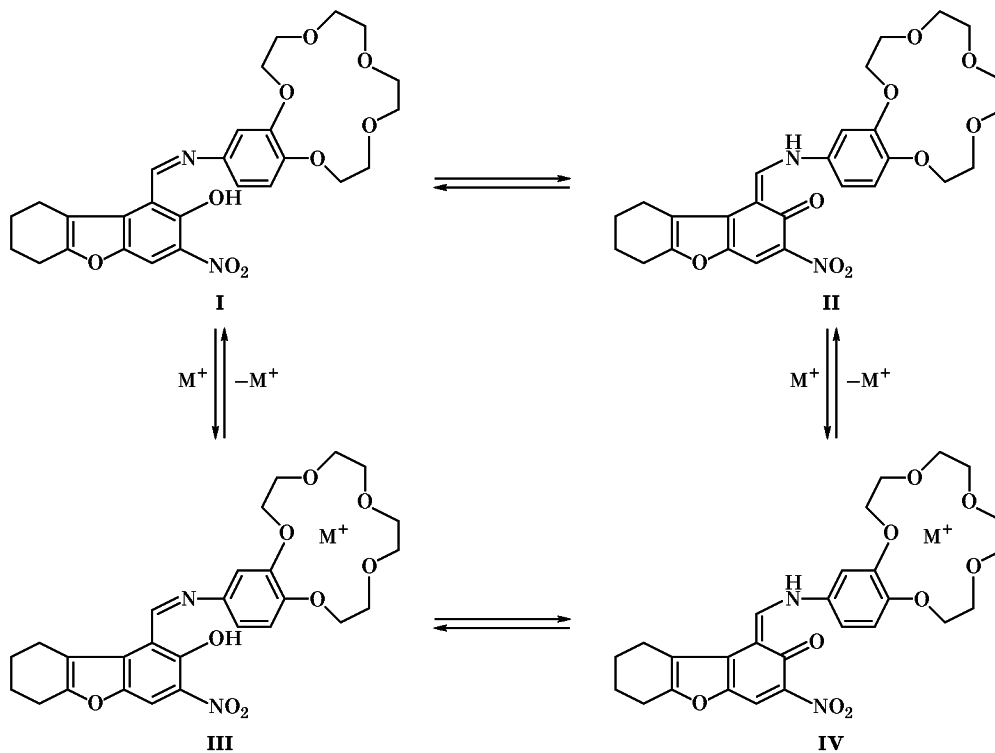
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The presence of a crown ether moiety in a chemosensor molecule can give rise to considerable variation in its absorption and luminescence properties on complex formation with metal cations [1–3]. How-

ever, there are no published data on the effect of crown ether fragment on the state of tautomeric equilibrium in benzoid–quinoid systems which can be used as dynamic fluorescent sensors for metal cations.

Scheme 1.



$M = Li^+, Na^+, K^+, Cs^+$.

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With the goal of obtaining such a system we have synthesized Schiff base **I** (Scheme 1) and examined its absorption and luminescence properties.

Like related Schiff bases having no crown ether moiety [4], compound **I** in solution gives rise to tautomeric equilibrium **I** \rightleftharpoons **II** between the benzoid (**I**, $\lambda_{\max} = 360\text{--}370$ nm) and quinoid forms (**II**, $\lambda_{\max} = 460$ nm) with the following constants $K^0 = [\text{II}]/[\text{I}] = 0.03$ (toluene), 0.33 (acetonitrile). Addition of a metal iodide solution leads to appearance of new equilibrium **III** \rightleftharpoons **IV** which is characterized by decrease of the fraction of quinoid tautomer **IV** in the series $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. The state of the benzoid–quinoid equilibrium in dimethyl sulfoxide is influenced to an appreciable extent only by Li^+ ion: in this case the fraction of tautomer **IV** increases. The absorption parameters of model Schiff bases having no crown ether fragment did not change in the presence of Li^+ ion. Excitation of Schiff base **I** in acetonitrile at the absorption maximum of the benzoid form ($\lambda_{\text{excit}} = 370$ nm) induces a strong fluorescence at $\lambda = 560$ nm with an anomalous Stokes shift ($\Delta\nu = 8459$ cm^{-1}), which arises from intramolecular proton transfer in the excited state [5]. Addition of lithium iodide to this solution leads to a blue shift of the fluorescence band (to $\lambda = 550$ nm; $\Delta\nu = 8134$ cm^{-1}).

These specific changes in the absorption and luminescence properties, occurring on complex formation, allow us to consider the system under study to be the first example of fluorescent tautomeric benzoid–quinoid sensor for metal cations.

5-Hydroxy-6-nitro-4-(2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-1(15),16,18-trien-17-ylimino-methyl)-2,3-tetramethylenebenzo[*b*]furan (I**)** was synthesized by the procedure reported in [4] from

4-aminobenzo-15-crown-5 and 5-hydroxy-6-nitro-2,3-tetramethylenebenzo[*b*]furan-4-carbaldehyde. The product was recrystallized from ethanol. Yield 68%. Yellow powder, mp 164°C. IR spectrum (mineral oil), ν , cm^{-1} : 1590, 1630. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.93–1.95 m (4H, 2CH₂), 2.80–2.83 m (4H, 2CH₂), 3.62–4.17 m (16H, 8CH₂O), 6.88–7.24 m (3H, H_{arom}), 8.22 s (1H, 7-H), 9.00 s (1H, CHN), 16.43 s (1H, OH). Electron absorption spectrum (in acetonitrile), λ_{\max} , nm ($\epsilon \times 10^{-3}$, $1 \text{ mol}^{-1} \text{ cm}^{-1}$): 377 (23.6), 490 (4.4). Found, %: C 61.38; H 5.71; N 5.55. $\text{C}_{27}\text{H}_{30}\text{N}_2\text{O}_9$. Calculated, %: C 61.59; H 5.74; N 5.32.

The ^1H NMR spectrum was taken on a Varian Unity 300 instrument (300 MHz) relative to TMS as reference. The IR spectrum was recorded on a Specord 75IR spectrometer. The electron absorption spectra were measured on a Specord M-40 spectrophotometer.

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