

Photoinduced Acylotropic Rearrangement of Crown-Containing 2-[N-Acetyl-N-(4-aminobenzo-15-crown-5)methylene]-2,3-dihydrobenzo[b]thiophen-3-one*

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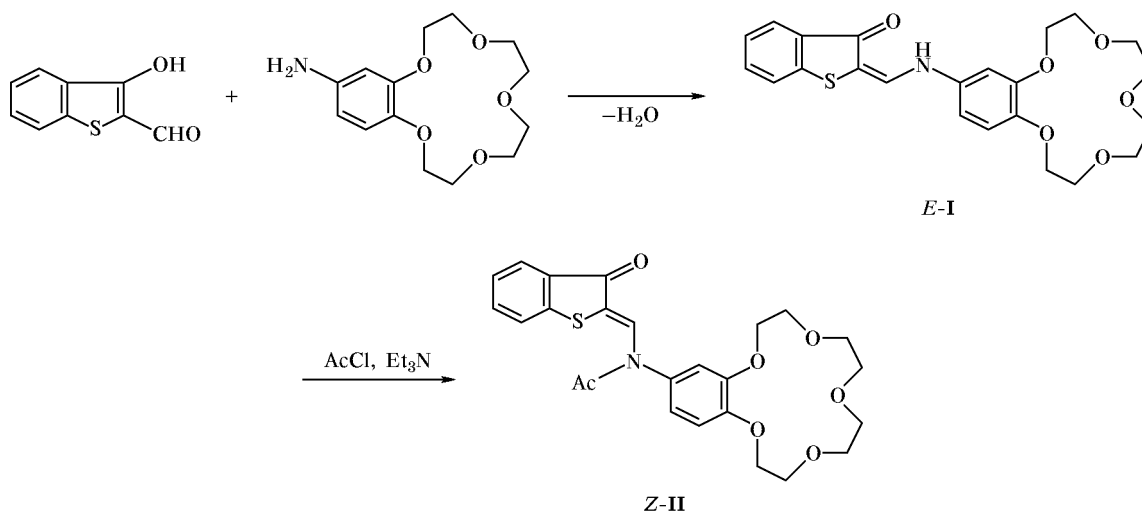
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Abstract—2-N-(4-Aminobenzo-15-crown-5)methylene-2,3-dihydrobenzo[b]thiophen-3-one and its acetyl derivative were synthesized. Their treatment with lithium, sodium, or potassium iodide in acetonitrile solution leads to formation of the corresponding crown–metal complexes. Irradiation of the acylated compounds at λ 436 nm induces N \rightarrow O migration of the acetyl group to give O-acyl isomer which is characterized by a considerable blue shift of the long-wave absorption band ($\Delta\lambda = 70$ nm). The quantum yields of the photoinduced acylotropic reaction for the free ligand and its complexes with alkali metal cations change in the series: $\varphi_L > \varphi_{K^+} > \varphi_{Na^+} > \varphi_{Li^+}$.

Introduction of a crown-ether moiety into molecules of photochromic compounds could lead to considerable variation of its spectral and photochemical properties on complex formation with metal cations [1–3]. Compounds having a crown receptor can be

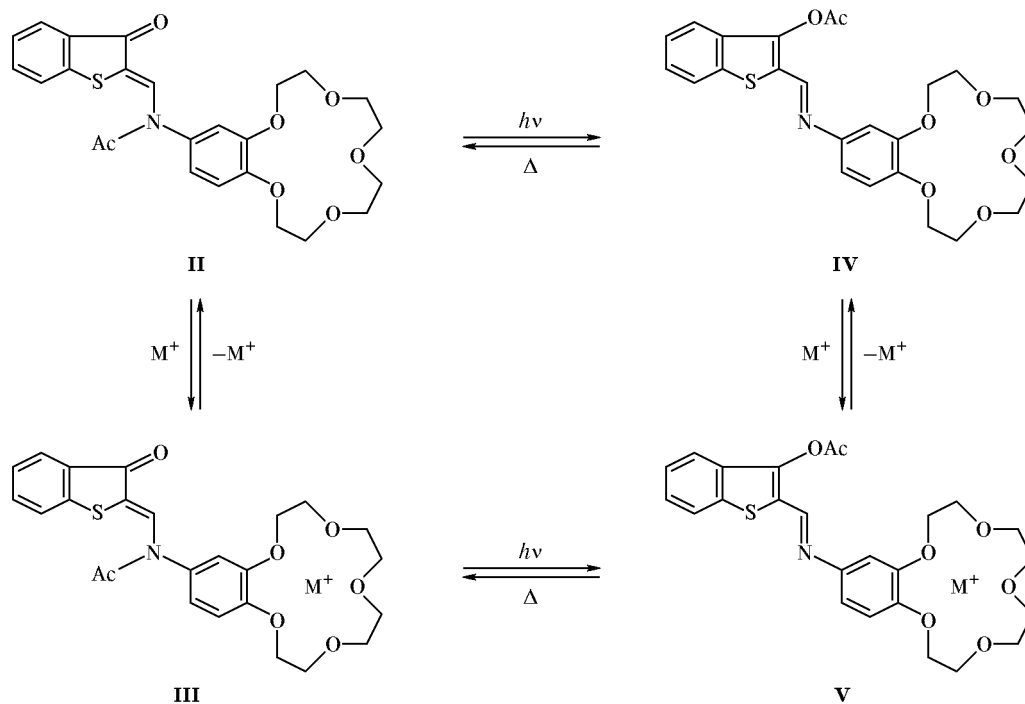
used in the design of organic molecular switches, data storage systems, and chemosensors for biologically important ions [4, 5]. Most of the previously studied compounds of this kind belong to the spirooxazine or spiropyran series or are capable of undergoing photo-

Scheme 1.



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Scheme 2.



induced *E/Z* isomerization. In the present communication we report for the first time on a crown-containing aminovinyl ketone system (**I**) and its *N*-acetyl derivative (**II**) which give rise to photoinduced acylotropic $N \rightarrow O$ rearrangement.

Compound **I** was synthesized by condensation of 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde with 4-aminobenzo-15-crown-5. Acylation of **I** with acetyl chloride in the presence of excess triethylamine gave *N*-acetyl derivative **II** (Scheme 1). The structure of products **I** and **II** was proved by the UV, IR, and ^1H NMR spectra (see Experimental). The *E* configuration of the aminovinyl ketone fragment follows from the position of the long-wave absorption maximum in the electron spectrum (λ 450 nm), which is typical of such systems, as well as from the presence of a carbonyl absorption band at 1640 cm^{-1} in the IR spectrum and a downfield signal (δ 12.4 ppm) of the NH proton in the ^1H NMR spectrum [6, 7]. *Z* Isomer **II** is characterized by the long-wave absorption maximum with a specific shape, located at λ 430 nm; in the IR spectrum of **II** we observed two carbonyl absorption bands at 1710 and 1660 cm^{-1} , and the CH proton signal appeared in the ^1H NMR spectrum at δ 8.9 ppm [8, 9]. Addition of lithium, sodium, or potassium iodide (5–10-fold excess) to a solution of compound **I** or **II** in acetonitrile induces small but characteristic changes in the electron absorption spectra ($\Delta\lambda = 1\text{--}4\text{ nm}$, $\Delta\epsilon = 5\text{--}15\%$). The blue shift of the long-

wave absorption band of **I** (λ_{max} 452 nm) or **II** (λ_{max} 430 nm) is accompanied by hypochromic effect; the absorption maxima at λ 340 nm (**I**) and 310 nm (**II**) are also displaced to the short-wave region, but their intensity increases. The electron absorption spectra of 2-*N*-(4-methoxyphenyl)aminomethylene-2,3-dihydrobenzo[*b*]thiophen-3-one and its *N*-acetyl derivative, which can be regarded as molecular models of compounds **I** and **II** with no crown-ether moiety, almost does not change on addition of alkali metal salts.

Appreciable variations in the spectral and photochemical properties were observed on irradiation of *N*-acylated aminovinyl ketone **II** and its complexes **III**. Irradiation of compounds **II** and **III** at the long-wave absorption maximum (λ_{irr} 436 nm) induces transfer of the acetyl group from the nitrogen to carbonyl oxygen atom with formation of *O*-acetyl isomers **IV** and **V**. The process is accompanied by appearance of new absorption bands in the range λ 360–370 nm (**IV**) and 355 nm (**V**) (Fig. 1). Photoinduced isomers **IV** and **V** are stable in solution for a long time; the reverse $O \rightarrow N$ rearrangement can be initiated by heating [8]. Increase in the intensity of the long-wave absorption maximum of complex **V** is especially characteristic of the lithium compound, $\epsilon_{\text{max}} = 1.14 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-1}$. This effect is weaker for the sodium ($\epsilon_{\text{max}} = 1.06 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-1}$) and potassium complexes ($\epsilon_{\text{max}} = 1.04 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-1}$);

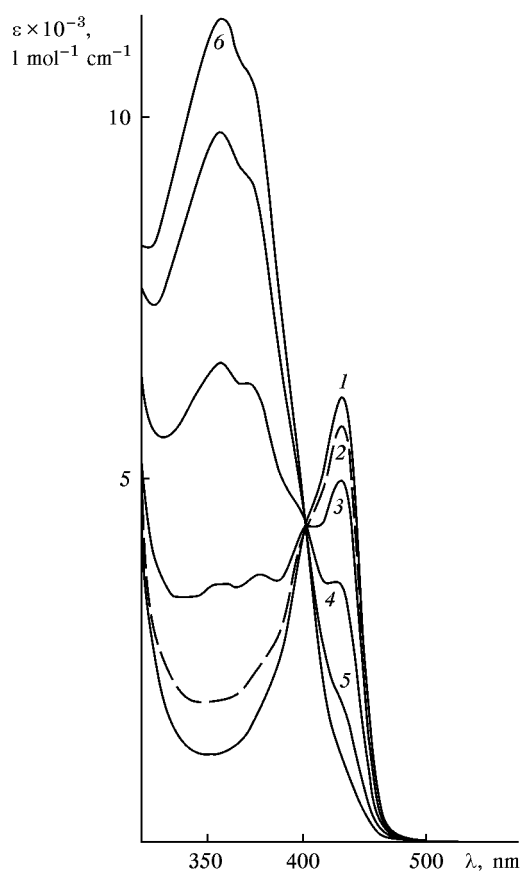


Fig. 1. Electron absorption spectra of compound **III** in acetonitrile in the presence of 10 equiv of LiI (1) before irradiation and after irradiation for (2) 5 s, (3) 10 s, (4) 20 s, (5) 40 s, and (6) 60 s; λ_{irr} 436 nm.

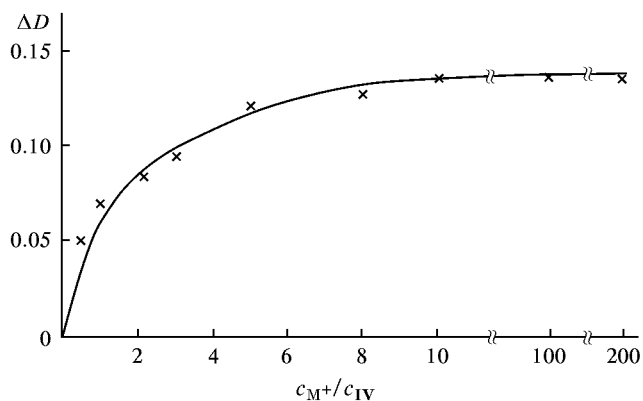


Fig. 2. Plot of ΔD for the lithium complex **V** versus concentration ratio of LiI and ligand **IV**.

the corresponding value for ligand **IV** is $1.00 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The quantum yields of the photochemical transformation **III** \rightarrow **V** strongly depend on the cation nature and are as follows: $\varphi = 0.33$ (**II**), 0.30 (**III**_{K⁺}), 0.23 (**III**_{Na⁺}), 0.12 (**III**_{Li⁺}).

With a view to check the applicability of the above transformations for quantitative determination of Li⁺ ions in solution we plotted the variation of ΔD at λ 357 nm corresponding to the absorption maximum of complex **V** on addition of LiI to irradiated solution of *O*-acetyl form **IV** ($c_{\text{IV}} = 6.55 \times 10^{-5} \text{ M}$; Fig. 2). The maximal value of ΔD was attained at a 10-fold excess of lithium iodide, and it increased insignificantly on further raising the concentration of LiI.

Thus, migration of the acyl group in the photo-induced reaction **II** \rightarrow **IV** leads to formation of species which are the most sensitive to complex formation. Therefore, system **II** can be regarded as a photochromic chemosensor for alkali metal cations, especially for Li⁺ ions.

EXPERIMENTAL

The electron absorption spectra were measured on a Specord M-40 spectrophotometer. Compounds **II** and **III** were irradiated in acetonitrile using a DRSh-250 mercury lamp with a set of light filters. The quantum yields were determined using 2-(*N*-acetyl-*N*-phenylaminomethylene)-2,3-dihydrobenzo[*b*]thiophen-3-one as reference [9]. The IR spectra were taken on a Specord IR-75 spectrometer. The ¹H NMR spectra were obtained on a Varian Unity-300 instrument (300 MHz) in CDCl₃ using an external reference.

2-*N*-(4-Aminobenzo-15-crown-5)methylene-2,3-dihydrobenzo[*b*]thiophen-3-one (I) was synthesized by condensation of equimolar amounts of 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde and 4-aminobenzo-15-crown-5, following the procedure described in [6]. The product was recrystallized from ethanol. Yield 70%. Red powder, mp 193°C. IR spectrum (mineral oil), ν , cm⁻¹: 1640, 1560. ¹H NMR spectrum, δ , ppm: 3.64 s (8H, 4CH₂O), 3.82 m (4H, 2CH₂O), 4.20 m (4H, 2CH₂O), 6.7–7.9 m (8H, H_{arom}), 8.0 d (1H, CH), 12.4 m (1H, NH). UV spectrum (CH₃CN), λ_{max} , nm ($\epsilon \times 10^{-3}$, l mol⁻¹ cm⁻¹): 340 (9.1), 452 (17.6). Found, %: C 62.41; H 5.65; N 3.22. C₂₃H₂₅NO₆S. Calculated, %: C 62.29; H 5.68; N 3.16.

2-[*N*-Acetyl-*N*-(4-aminobenzo-15-crown-5)-methylene]-2,3-dihydrobenzo[*b*]thiophen-3-one (II) was obtained by acylation of compound **I** with acetyl chloride in the presence of excess triethylamine, following the procedure described in [9]. The product was recrystallized from toluene. Yield 82%. Yellow crystals, mp 176°C. IR spectrum (mineral oil), ν , cm⁻¹: 1710, 1660, 1600. ¹H NMR spectrum, δ , ppm: 2.10 s (3H, CH₃), 3.80 s (8H, 4CH₂O), 3.95 m (4H, 2CH₂O), 4.20 m (4H, 2CH₂O), 6.7–7.9 m (8H, H_{arom}), 8.9 s (1H, CH). UV spectrum (CH₃CN), λ_{max} , nm

($\epsilon \times 10^{-3}$, $1 \text{ mol}^{-1} \text{ cm}^{-1}$): 310 (9.7), 430 (6.4). Found, %: C 70.04; H 5.27; N 2.86. $\text{C}_{25}\text{H}_{27}\text{NO}_7\text{S}$. Calculated, %: C 61.97; H 5.41; N 2.89.

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