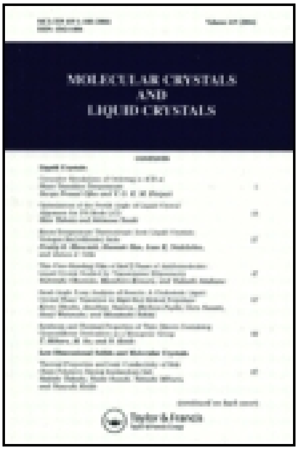

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Photochromic Cation Sensors

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Photochromic Cation Sensors

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Novel photochromic chemosensors for alkali-, alkali-earth and d-metal cations were synthesized and their photochemical and complexing properties investigated with the use of UV/vis, IR, $^1H/^7Li$ NMR spectroscopy and quantum chemical calculations–DFT(B3LYP/6-31G).

Keywords: chemosensors; ketoenamines; photochromism

INTRODUCTION

N-Acylated ketoenamines **1** are the basic components of the efficient abiotic solar energy storage system [1]. A proper modification of the structure of these compounds imparts to them the properties of molecular switches [2,3], photocromic pH-sensors [4] or chemosensors for metal cations [5]. In order to further explore the last possibility we have synthesized and investigated properties of benzo-15-crown-5-containing ketoenamines **1a–c**.

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EXPERIMENTAL

UV/Vis absorption spectra were measured with a Specord M-40. IR spectra were recorded on a Specord 75IR in nujol. ^{1}H and ^{7}Li NMR spectra were recorded using Varian Unity 300 (300 MHz) spectrometer.

For the irradiation of solutions of **1a–c** a high-pressure mercury lamp DRSh (250 W) has been used supplied with a set of glass filters. Potassium ferrioxalate was used as an actinometer for the determination of quantum yields of the photoreations [6].

The synthesis of compounds **1a,b** has been described in a previous work [2]. 2-{N-Phenylthioacetyl-N-[(benzo-15-crown-5)-4′-yl]aminomethylene}benzo[b]thiophene-3(2H)-one (**1c**). 2-{N-[(Benzo-15-crown-5)-4′-yl]aminomethylene-3(2H)-one (1 mmol) [2] was dissolved in 3 ml of acetonitrile in the presence of triethylamine and a solution of 1.2 mmol of phenylthioacetylchloride in 2 ml of acetonitrile was added at room temperature. The precipitate formed was filtered off and crystallized from toluene to give 0.71 mmol (71%) of **1c** yellow powder.

M.p. 201–202°C. Found: C 62.78; H 5.35; N 2.34; S 10.85%. $C_{31}H_{31}NO_7S_2$ requires: C 62.68; H 5.26; N 2.27; S 10.80%.

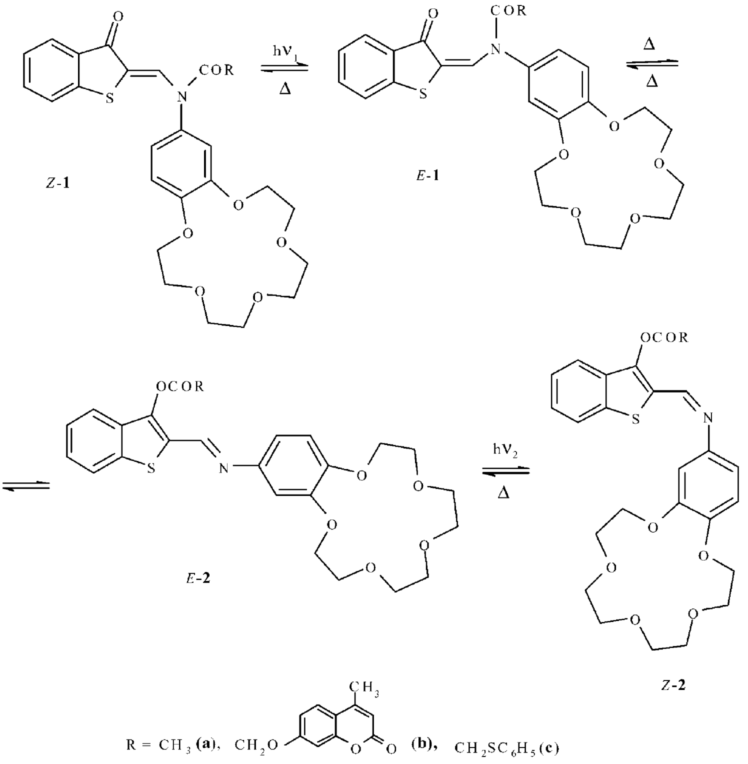
^{1}H NMR (CD_3CN, δ, ppm), 3.53–3.64 (s, 2H, CH_2), 4.29–4.71 (m, 16H, $8CH_2O$), 6.72–7.84 (m, 12H, arom.), 8.84–8.88 (s, 1H, CH=).

IR (Nujol, ν, cm^{-1}): 1690, 1670.

RESULTS AND DISCUSSION

The structures of ketoenamines **1a–c** correspond to the N-acyl forms, which is evidenced by their IR spectra displaying the characteristic amide (1690–1710 cm^{-1}) and exocyclic thiophene carbonyl (1650–1670 cm^{-1}) group vibration bands. The low-field resonance ^{1}H NMR signals of the methine protons 8.7–8.9 ppm [1] indicate *Z*-configuration about the C=C bond. Irradiation of acetonitrile solutions of **1a–c** with 436 nm filtered light results in *Z*/*E*-isomerization around the C=C bond followed by the thermal N→O acyl migration with the formation of O-acyl isomers **2a–c**. The quantum yields of the reactions were determined as follows 0.25 (**a**), 0.48 (**b**) and 0.40 (**c**) (Scheme 1).

The rearrangement is accompanied by the substantial decrease in the initial intensity of 430–440 nm band and the appearance of a new absorption band at the 350–360 nm region. Simultaneously the ester carbonyl group band at 1780–1790 cm^{-1} (in CCl_4) appears in the IR spectra of **2a–c**. Irradiation of O-acyl derivatives **2a–c** (λ_{irr} 365 nm) causes thermally reversible E/Z-isomerization around the C=N bond.

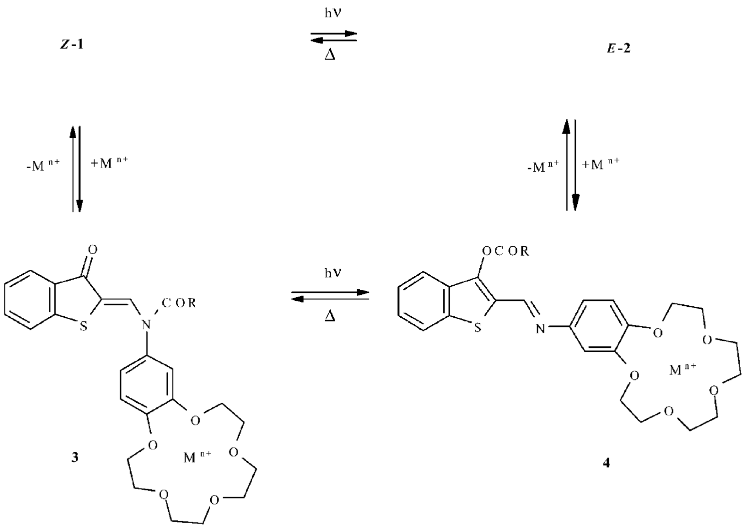


SCHEME 1 Photochemical and thermal isomerizations of compounds **1** and **2**.

The UV/Vis absorption spectra of the initial crown-containing compounds **1a–c** exhibit very small changes in the presence of alkali-, alkali-earth- and d-metal cations. In contrast, the O-acyl isomers **2** obtained by the photochemical rearrangement form with the cations complexes **4** which display substantial changes in the intensity of 350–360 nm bands (increase of the extinction $\Delta\varepsilon$) and blue shifts $\Delta\lambda$ (Scheme 2, Table 1).

The formation of the crown-ether complexes **4** was justified by the ^{1}H and ^{7}Li NMR spectral data: methylene proton signals of the crown ring are 0.06–0.10 ppm low-field shifted in **4** as compared with **2**. The protons more distant from the crown moiety do not measurably respond to the presence of M^{n+} in the crown-ether ring. In the ^{7}Li NMR spectra of **4** ($M^{n+} = Li^{+}$), the lithium resonance is 0.70–0.78 ppm shifted to the low field with respect to that of LiI.

Therefore, the compound **1a** represents a photochromic chemosensor which after irradiation converts to its isomer **2a** exhibiting unique



SCHEME 2 Photochemical and thermal isomerizations of compounds **Z-1**, **E-2**, **3** and **4** in the presence of M^{n+}.

selectivity to lithium cation in acetonitrile solution. The specific absorption changes ($\Delta\varepsilon$, $\Delta\lambda$) (Table 1) are not influenced by the presence in the solution of other alkali-metal ions in the comparable concentration. The rearrangement of **2b** produces the isomeric form **4b** which shows specific activity with respect to alkali-earth metal cations (Table 1, Figure 1), probably, due to the double coordination of M^{2+} by the crown-ether ring and 4-methyl-1,2-benzopyrone-7-yloxyacetic

TABLE 1 Spectral Changes in the 350–360 nm Absorption Band of Complexes **4** as Compared with **2** and Quantum Yields (φ) of the **3** → **4** Photorearrangements in an Acetonitrile Solution in the Presence of M^{n+}

Compound	**4a**			**4b**			**4c**		
M^{n+}	$\Delta\varepsilon$, %	$\Delta\lambda$, HM	φ	$\Delta\varepsilon$, %	$\Delta\lambda$, HM	φ	$\Delta\varepsilon$, %	$\Delta\lambda$, HM	φ
Li^+	13.1	10	0.43	12.9	9	0.62	20.9	14	0.54
Na^+	10.9	8	0.39	7.5	8	0.55	14.1	12	0.49
K^+	7.2	7	0.39	5.9	8	0.54	13.0	10	0.48
Cs^+	5.5	5	0.29	4.8	4	0.49	7.65	2	0.41
Mg^{2+}	29.4	19	0.32	76.3	57	0.62	35.5	18	0.67
Ca^{2+}	33.3	16	0.39	79.0	57	0.73	38.0	20	0.64
Sr^{2+}	23.5	16	0.37	69.9	55	0.49	22.6	16	0.63
Ba^{2+}	28.6	16	0.45	76.2	55	0.50	24.3	18	0.61

moiety [7]. Under irradiation, phenylthioacetyl derivative **1c** rearranges into the isomeric form **2c** which properties with respect to IA and IIA sub-group metal cations resemble those of **2a**, but **2c** also shows significant activity with respect to some d-metal cations: Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} ($\Delta\varepsilon \leq 30\%$).

The selectivity of **2a** with respect to lithium cation can't be explained on the basis of the structural conformity principle [8], according to which 15-crown-5-ether is the most suitable host for Na^+ due to the geometrical parameters. We have computationally studied the complexation reaction of a model compound **5** with Li^+, Na^+ and K^+ cations using the DFT method (B3LYP/6-31G) [9].

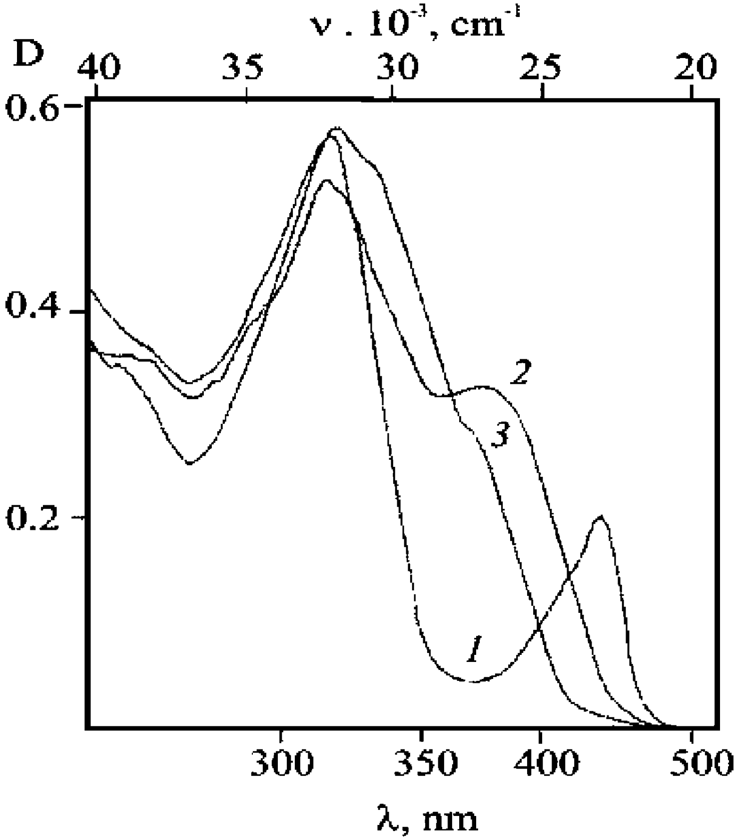
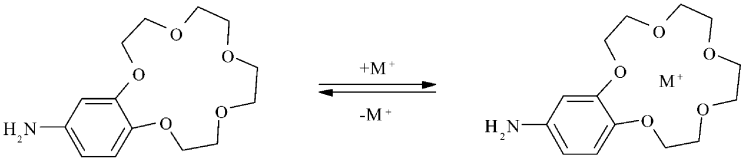


FIGURE 1 Absorption spectra of 2-{N-(4-methyl-1,2-benzopyrone-7-yloxyacetyl)-N-[(benzo-15-crown-5)-4′-yl]aminomethylene}benzo[b]thiophene-3(2H)-one (**1b**) in acetonitrile before irradiation (1), after 120 s of irradiation (2) (λ_{irr} =436 nm) and after addition of $Ca(ClO_4)_2$ (3); C = $1.7{\cdot}10^{-5}$ M.



5

M = Li (**6**), Na (**7**), K (**8**)

The results of the quantum-chemical calculations clearly evidence the decrease in the energy of orbital interaction between the crown-ether oxygen atoms and the vacant *p*-orbitals of M^+ in the sequence: **6** (43.3 kcal/mol), **7** (24.5 kcal/mol), **8** (11.9 kcal/mol). This effect is explained by the increase this sequence of energy splitting between the orbitals of interacting components.

CONCLUSIONS

A series of N-acylated benzo-15-crown-containing ketoenamines **1a–c** has been prepared and showed the properties of a new type of photochromic chemosensors with respect to IA sub-group (acetyl derivative **1a**), IIA sub-group (4-methyl-1,2-benzopyrone-7-yloxyacetyl derivative **1b**) and d-metal cations (phenylthioacetyl derivative **1c**).

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