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Benzoid–Quinoid Tautomerism of Schiff Bases and Their Structural Analogs: LI.* Photoacylotropic Enaminoketones with a Fluorophoric Migrant**

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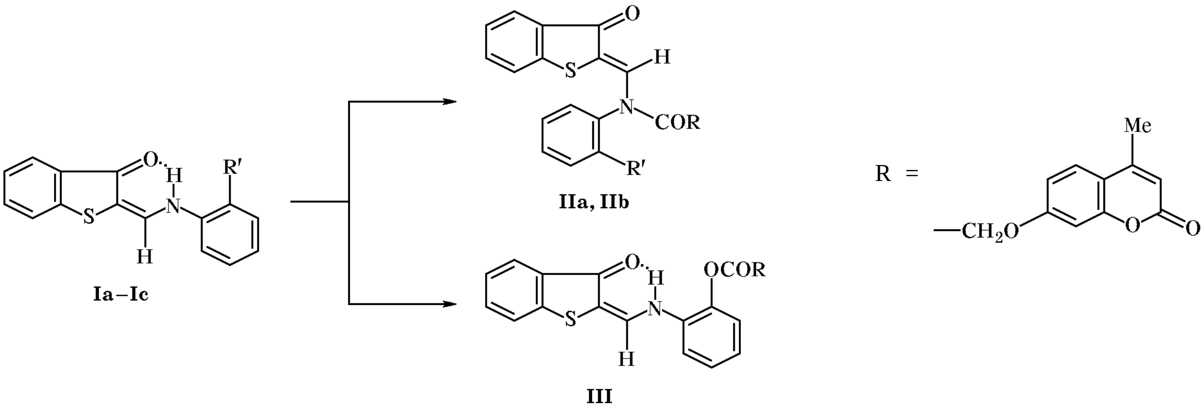
Abstract—The acylation of *ortho*-substituted (R = OH, OMe, NHTs) 2-arylaminomethylene-2,3-dihydrobenzo[*b*]thiophen-3-ones with (4-methyl-2-oxobenzo[*b*]pyran-7-yloxy)acetyl chloride results in formation of the corresponding *N*-acyl enaminoketones. The same reaction with 2-(2-hydroxyphenylaminomethylene)-2,3-dihydrobenzo[*b*]thiophen-3-one gives rise to a tautomeric mixture of acyloxyphenyl and *N*-acyl enaminoketone isomers. Irradiation at a wavelength corresponding to the absorption region of the *N*-acyl enaminoketone isomer leads to N→O acyl group transfer to afford O-acylated isomer. The complex formation ability of all tautomeric forms with respect to Zn^{2+} and Ni^{2+} cations and their fluorescence properties were studied.

The ability of N-acylated enaminoketones to undergo photoinduced acylotropic rearrangements [2] provides the possibility for creation of photochromic fluorescent sensors for metal cations if the molecule contains fluorescence and complexing centers [3, 4]. The present communication reports on the synthesis and properties of *ortho*-substituted *N*-aryl Schiff bases derived from 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde and modified through introduction of a fluorophoric acyl migrant, (4-methyl-2-oxobenzo[*b*]pyran-7-

Scheme 1.



I, **II**, R′ = MeO (**a**), TsNH (**b**), HO (**c**).

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[*] For communication L, see [1].

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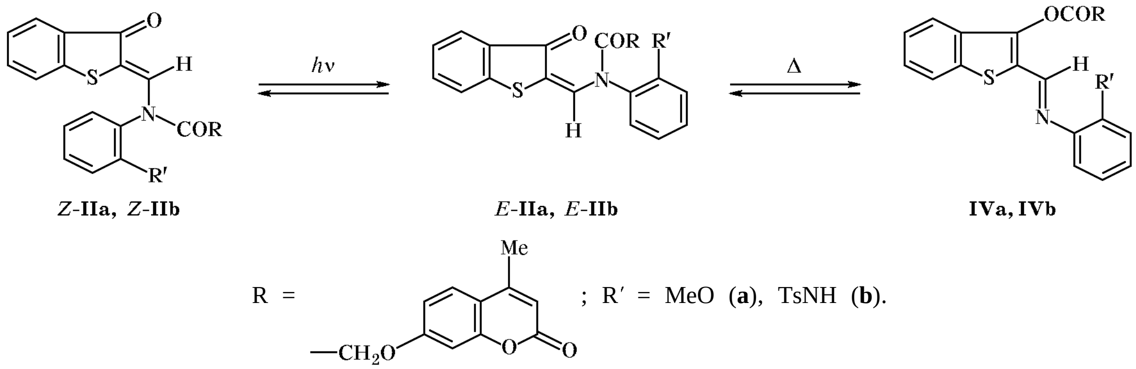
Scheme 2.

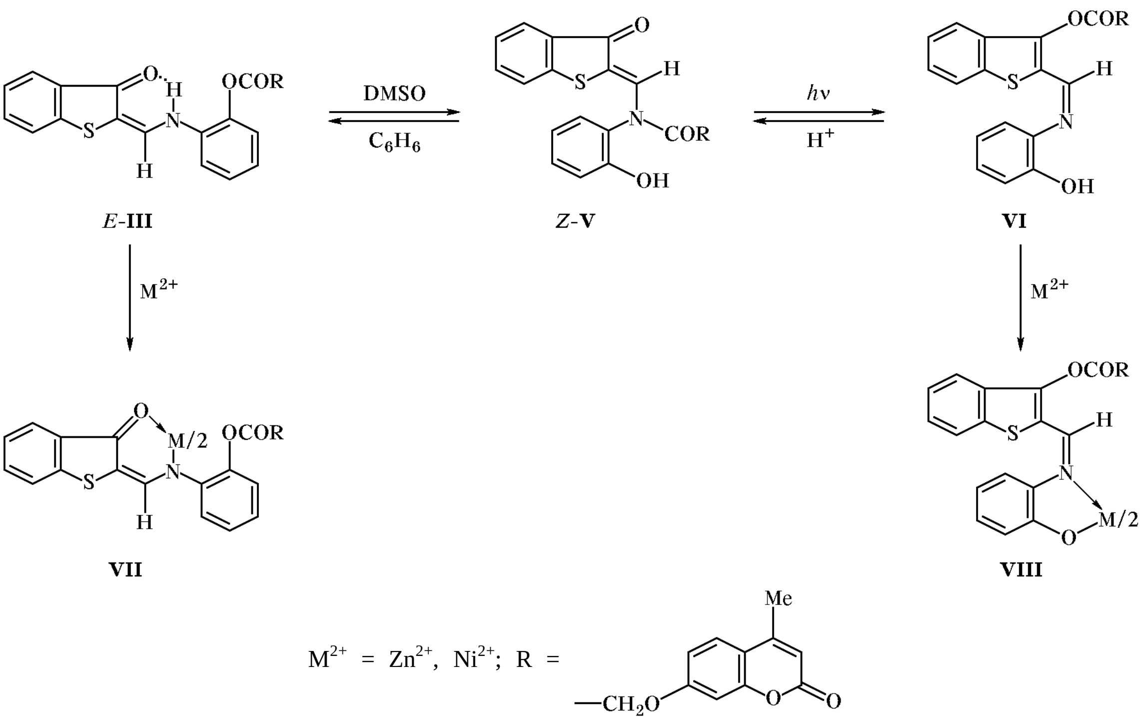


yloxy)acetic acid residue. Enaminoketones **Ia**–**Ic** were obtained by condensation of 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde [5] with *ortho*-substituted anilines, following the procedure described in [6]. The structure of **Ia**–**Ic** was confirmed by the IR and ^{1}H NMR spectra. The IR band at 1650 cm^{-1} corresponds to the ring carbonyl involved in a strong intramolecular hydrogen bond. However, the set of signals observed in the ^{1}H NMR spectra includes two pairs of doublets from the amine and methine protons, indicating the presence of both *E* and *Z* isomers [7]. By the action on compounds **Ia**–**Ic** of (4-methyl-2-oxobenzo[*b*]pyran-7-yloxy)acetyl chloride we obtained acylated enaminoketones **IIa**, **IIb**, and **III** (Scheme 1).

The structure of compounds **IIa** and **IIb** as *Z*-enaminoketones is confirmed by the presence in the IR spectra of absorption bands of the amide (1710 cm^{-1}) and endocyclic carbonyl groups (1650 cm^{-1}), as well as by a characteristic chemical shift of the methine proton (δ 9.2 ppm) [2] in the ^{1}H NMR spectrum. The enaminoketone structure of compound **III** in crystal was derived from the IR spectrum which contained the following absorption bands: 1760 (ester carbonyl), 1640 (exocyclic carbonyl group), 1630 (lactone carbonyl in the pyran ring), and 3350 cm^{-1} (strongly broadened νN–H band).

Scheme 2 illustrates transformations of *N*-acylated enaminoketones **IIa** and **IIb** on irradiation in solution

Scheme 3.



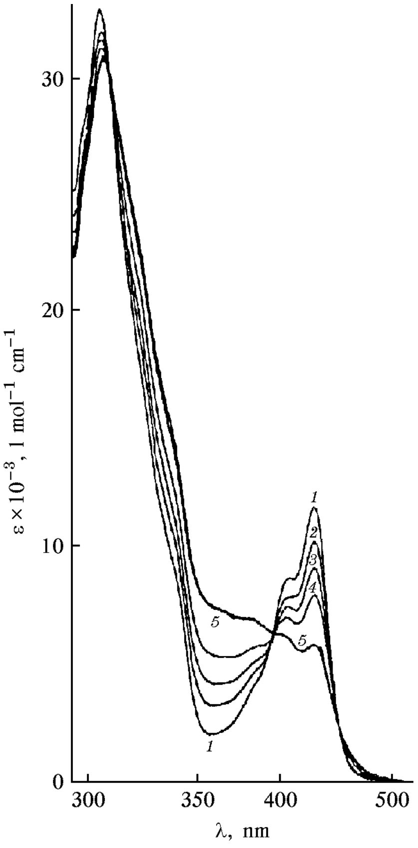


Fig. 1. Electron absorption spectra of enaminoketone **IIa** in toluene (*1*) before irradiation and after irradiation for (*2*) 10 s, (*3*) 20 s, (*4*) 1 min, and (*5*) 2 min (λ_{exc} 436 nm).

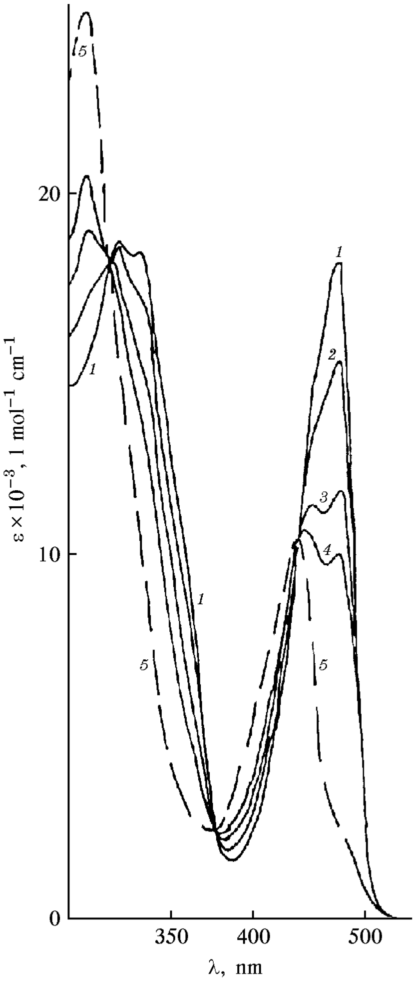


Fig. 2. Electron absorption spectra of enaminoketone **III** (*1*) in toluene, in toluene containing (*2*) 2.4, (*3*) 4.8, and (*4*) 7% of DMSO, and (*5*) in DMSO.

[2, 8]. Structures *Z*-**IIa** and *Z*-**IIb** show a characteristic maximum at λ 418–428 nm in the electron absorption spectrum. Irradiation at that band (λ_{exc} 436 nm) induces fast *Z*,*E* isomerization of compounds **IIa** and **IIb** with subsequent thermal N→O transfer of the acyl group and formation of *O*-acyl isomers **IVa** and **IVb** which absorb at 360–370 nm. However, unlike most previously studied analogs, the photochemical transformation goes until equilibrium (Scheme 2) establishes between the *N*- and *O*-acyl isomers (Fig. 1). The state of the equilibrium strongly depends on the solvent nature and compound structure: polar solvents stabilize *O*-acyl form **IVa** or *N*-acyl form **IIb**. The equilibrium constants K^0 = [**IV**]/[**II**] and Gibbs energies ΔG^0_{294} are given in table. In the presence of CCl_3CO_2H the equilibrium is displaced completely toward initial isomer *Z*-**IIa** and *Z*-**IIb**.

Thermodynamic parameters of the equilibria involving compounds **IIa** and **IIb**

Solvent	K^0		ΔG^0_{294}, kJ/mol	
	IIa	**IIb**	**IIa**	**IIb**
Toluene	1.04	7.3	–0.001	–4.7
Acetonitrile	1.63	1.03	–1.15	–0.001
DMSO	[a]	0.07	[a]	6.3

[a] Irradiation of compound **IIa** in DMSO at λ_{exc} 436 nm induces both acylotropic N→O migration and partial decomposition.

Compound **III** in solution gives rise to a dynamic equilibrium between the enaminoketone (*E*-**III**) and *N*-acyl forms (*Z*-**V**) in the ground state (Scheme 3). In nonpolar solvents, such as hexane, benzene, and toluene, the equilibrium is displaced toward isomer

E-**III** which is stabilized by intramolecular hydrogen bond; it absorbs in the region of 470 nm (Fig. 2, *1*), which is typical of enaminoketones of the benzo[*b*]-thiophene series [6]. In polar solvents like DMSO the equilibrium shifts almost completely toward the *N*-acylated form (*Z*-**V**) whose absorption maximum is located at λ 432 nm (Fig. 2, *5*). Assuming that the molar absorption coefficient at λ_{max} 470 nm corresponds to the pure tautomer *E*-**III**, about 15% of *E*-**III** remains in the solution and 85% of *Z*-**V** appears.

The presence of *N*-acyl isomer *Z*-**V** in the mixture makes it possible to effect photoinduced rearrangement of *Z*-**V** into **VI**. In fact, irradiation of solutions of **III** in polar solvents at λ_{exc} 436 nm leads to formation of *O*-acyl isomer **VI** which absorbs at λ 440–460 nm. However, as with compounds **IIa** and **IIb**, the fraction of **VI** does not reach 100% but a multicomponent equilibrium involving all possible isomers establishes (Scheme 3). It is difficult to estimate the fractions of each particular isomer on the basis of electron absorption spectra, for bands of three of them strongly overlap. Study of the fluorescence spectra of compound **III** in toluene and in DMSO, as well as in the equilibrium mixture obtained after irradiation, shows that only one isomer (*E*-**III**) fluoresces, in agreement with the data of [9]. The shapes and positions of the fluorescence bands in different solvents are similar (λ_{max}^{fl} 490–550 nm; Fig. 3), but they strongly differ in intensity. Insofar as only isomer *E*-**III** is present in toluene, the fluorescence excitation spectrum almost coincides with the absorption spectrum (Fig. 3a, *3*). In dimethyl sulfoxide, fluorescence is induced by excitation in the region of 470 nm, which corresponds (see above) to a 15% fraction of *E*-**III** (Fig. 3b, *5*).

Addition of salts $M(OAc)_2$ to the equilibrium mixture (Scheme 3) could give rise to formation of two kinds of complexes, **VII** and **VIII**, whose absorption and fluorescence properties should differ considerably. However, regardless of the solvent polarity, addition of Zn^{2+} or Ni^{2+} ions before or after irradiation resulted in complete displacement of the equilibrium toward complex **VII**. This compound is characterized by a broadened long-wave absorption band in the region 440–510 nm and fluorescence band at λ_{max}^{fl} 510 nm.

Thus we have demonstrated the possibility, in principle, for creation of photochromic enaminoketone systems involving a fluorophoric migrant, which are capable of forming complexes with metal cations. Search for fluorescent sensors in this series of photochromic compounds will be continued through variation of the migrating group and creation of new complexing centers.

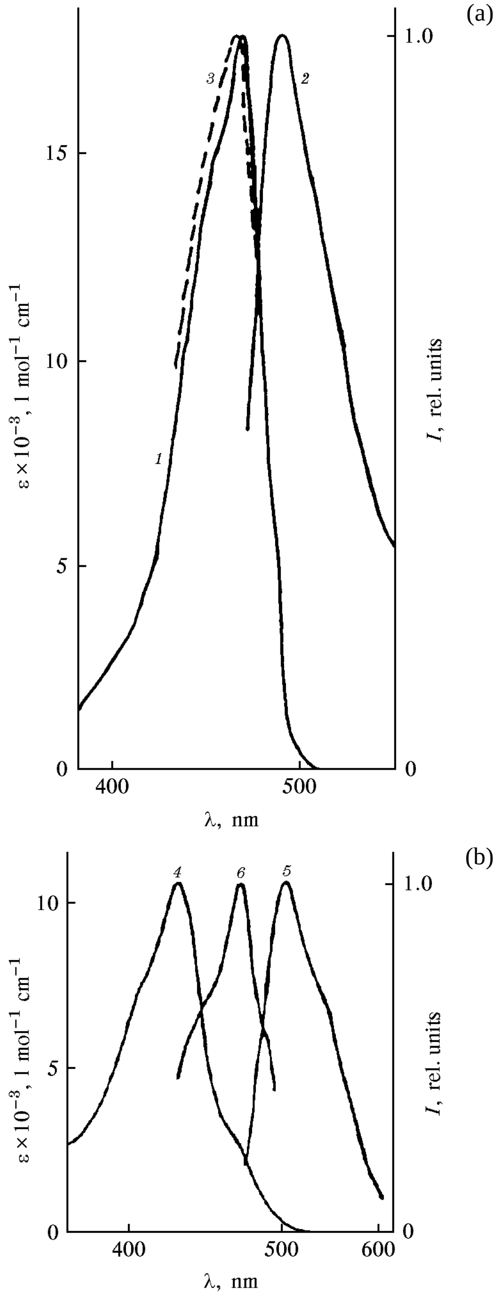


Fig. 3. Electron absorption and emission spectra of enaminoketone **III** in (a) toluene and (b) DMSO: (*1*, *4*) absorption, (*2*, *5*) fluorescence, (*3*, *6*) fluorescence excitation.

EXPERIMENTAL

The electron absorption spectra were measured on a Specord M-40 spectrophotometer. The fluorescence spectra were obtained on a Hitachi 650-60 spectrofluorimeter. Solutions of compounds **IIa**, **IIb**, and **III** were irradiated with a DRSh-250 mercury lamp using a set of removable light filters. The IR spectra were obtained from samples dispersed in mineral oil using a Specord 75IR spectrometer. The ^{1}H NMR spectra were recorded on a Varian Unity-300 instrument (300 MHz) in DMSO-d_6 with TMS as reference.

2-(2-Methoxyphenylaminomethylene)-2,3-dihydrobenzo[*b*]tiophen-3-one (Ia) was synthesized by the procedure described in [6] from 2-methoxyaniline and 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde. The product was recrystallized from toluene. Yield 92%, yellowish–brown crystalline substance, mp 163°C. Electron absorption spectrum (toluene), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l cm^{-1} mol^{-1}): 310 (32.7). 428 (11.6). Found, %: C 67.64; H 4.52; N 4.76. $C_{16}H_{13}NO_2S$. Calculated, %: C 67.82; H 4.62; N 4.94.

2-[2-(*p*-Tolylsulfonylamino)phenylaminomethylene)-2,3-dihydrobenzo[*b*]thiophen-3-one (Ib) was synthesized by the procedure described in [6] from 2-(*p*-tolylsulfonylamino)aniline and 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde. The product was recrystallized from 1-butanol–DMF (1 : 1). Yield 83%, yellow powder, mp 256°C. Electron absorption spectrum (toluene), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l cm^{-1} mol^{-1}): 307 (31.6), 424 (11.6). Found, %: C 62.35; H 4.19; N 6.53. $C_{22}H_{18}N_2O_3S_2$. Calculated, %: C 62.54; H 4.29; N 6.23.

2-(2-Hydroxyphenylaminomethylene)-2,3-dihydrobenzo[*b*]thiophen-3-one (Ic) was described previously [6].

(4-Methyl-2-oxobenzo[*b*]pyran-7-yloxy)acetic acid was synthesized by the procedure described in [10], by alkylation of 7-hydroxy-4-methylbenzo[*b*]-pyran-2-one with chloroacetic acid. Yield 67%, colorless crystalline substance, mp 212°C. IR spectrum, ν, cm^{-1}: 1750, 1630. ^{1}H NMR spectrum, δ, ppm: 2.4 s (3H, CH_3), 4.72 s (2H, CH_2), 6.12 s (1H, 3-H), 6.88 s (1H, 8-H), 6.94 d (1H, 6-H), 7.63 d (1H, 5-H, J = 6 Hz). Found, %: C 61.31; H 4.19. $C_{12}H_{10}O_5$. Calculated, %: C 61.54; H 4.30. The acid was converted into the corresponding chloride by the procedure described in [11]. (4-Methyl-2-oxobenzo[*b*]pyran-7-yloxy)acetyl chloride was isolated as a colorless crystalline substance. Yield 78%, mp 142°C.

Acylated enaminoketones IIa, IIb, and III. A solution of 1.2 mmol of (4-methyl-2-oxobenzo[*b*]pyran-7-yloxy)acetyl chloride in a minimal amount of anhydrous acetonitrile was added to a warm solution of 1 mmol of enaminoketone **Ia**–**Ic** in a minimal amount of anhydrous acetonitrile in the presence of triethylamine. The yellow precipitate was separated and recrystallized from appropriate solvent.

2-[*N*-(4-Methyl-2-oxobenzo[*b*]pyran-7-yloxyacetyl)-2-methoxyphenylaminomethylene]-2,3-dihydrobenzo[*b*]thiophen-3-one (IIa). Yield 66%, mp 243°C. Found, %: C 67.12; H 4.22; N 2.60. $C_{28}H_{21}NO_6S$. Calculated, %: C 67.32; H 4.24; N 2.80.

2-[*N*-(4-Methyl-2-oxobenzo[*b*]pyran-7-yloxyacetyl)-*N*-(2-*p*-tolylsulfonylaminophenyl)aminomethylene]-2,3-dihydrobenzo[*b*]thiophen-3-one (IIb). Yield 79%, mp 194°C. Found, %: C 63.78; H 4.07; N 4.16. $C_{34}H_{26}N_2O_7S_2$. Calculated, %: C 63.93; H 4.10; N 4.39.

2-[2-(4-Methyl-2-oxobenzo[*b*]pyran-7-yloxyacetyloxy)phenylaminomethylene]-2,3-dihydrobenzo[*b*]thiophen-3-one (III). Yield 61%, mp 221°C. Found, %: C 66.67; H 3.84; N 2.70. $C_{27}H_{19}NO_6S$. Calculated, %: C 66.79; H 3.94; N 2.89.

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