Russian Journal of Organic Chemistry, Vol. 38, No. 12, 2002, pp. 1813–1814. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 12, 2002, pp. 1872–1873.

SHORT COMMUNICATIONS

Molecular Switching and PET Effect in the Molecules of 2-(9-Anthrylmethylaminomethylene)benzo[*b*]thiophene and Its *N*-Acetyl Derivative*

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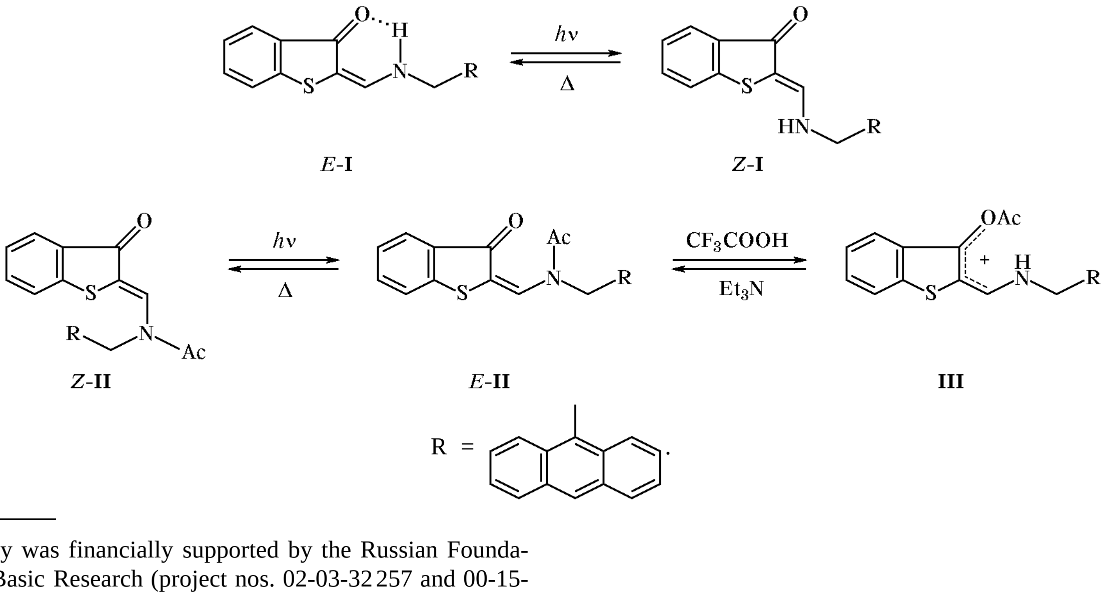
Received August 14, 2002

N-Acylated ketoenamine derived from benzo[*b*]thiophene and containing a benzo-15-crown-5 moiety is a photochromic chemosensor for metal cations [1]. On the other hand, it is known [2] that the presence of an *N*-fluorenone group in the amine fragment of a molecule makes the latter a fluorescent molecular switch. We made an attempt to synthesize a compound which would combine both these functions, molecular switch and sensor [3–6]. The molecules of ketoenamine **I** and its *N*-acetyl derivative **II** contain a 9-anthryl group whose fluorescence properties should be inhibited to a considerable extent as a result of photoinduced electron transfer (PET) [4, 6]. According to the IR, UV, and ^{1}H NMR spectral data, compound **I** exists mainly as *E* isomer (*E*-**I**) with respect to the exocyclic C=C bond, whereas its *N*-acetyl analog **II** has *Z*-configuration at the corresponding bond [1].

Irradiation of ketoenamine **I** in toluene at a wavelength corresponding to its long-wave absorption maximum (λ_{max} 438 nm) induces reversible (on heating) *E*/*Z* isomerization which is characterized by

Scheme 1.



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[*] This study was financially supported by the Russian Foundation for Basic Research (project nos. 02-03-32 257 and 00-15-97 320) and by CRDF–Ministry of Education of the Russian Federation (grant no. REC-004).

a blue shift of about 15 nm [7]. Under analogous conditions, *N*-acetyl derivative **III** (λ_{max} 428 nm) gives rise to thermally reversible *Z*/*E* isomerization without subsequent $N \rightarrow O$ acetyl group transfer (a red shift of about 5 nm is observed). Protonation of the *E* isomer of **II** with trifluoroacetic acid (5-fold excess) leads to rearrangement into *O*-acetyl isomer **III** (λ_{max} 338 nm) [8]. Neutralization of **III** with triethylamine recovers the initial compound with complete regeneration of the absorption spectrum.

Solutions of ketoenamine **I** in acetonitrile show a weak fluorescence at λ 455 nm ($\varphi \approx 0.01$); addition of CF_3COOH or Zn^{2+} enhances fluorescent properties due to weakening of PET (the fluorescence intensity increases by a factor of 5 or 3.5, respectively). The fluorescence properties of *N*-acetyl analog **II** are even weaker (λ_{max} 470 nm, $\varphi \approx 0.0025$). In the presence of Zn^{2+} ions, the efficiency of fluorescence increases by a factor of only 1.5, whereas addition of CF_3COOH leads to a 20-fold increase in the fluorescence intensity. No sensor activity of ketoenamine **II** for metal cations in toluene was observed, but addition of trifluoroacetic acid induces isomerization of **II** into compound **III** which is characterized by strong anthracene-like structuralized fluorescence (λ_{max} 415 nm, φ 0.33, 170-fold increase in intensity).

Thus ketoenamines **I** and **II** in acetonitrile exhibit sensor properties toward H^+ and Zn^{2+} ions due to weakening of PET. On irradiation in toluene at low pH ketoenamine **II** behaves as a fluorescent molecular switch.

2-(9-Anthrylmethylaminomethylene)benzo[*b*]thiophen-3(2*H*)-one (I). A solution of 0.72 g (3.5 mmol) of 9-aminomethylanthracene in 10 ml of acetonitrile was added to a warm solution of 0.62 g (3.5 mmol) of 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde in 10 ml of acetonitrile, and the mixture was heated to the boiling point. After cooling, the precipitate was filtered off and recrystallized from butanol. Yield 0.93 g (72%). Yellow powder with mp 192–193°C. IR spectrum, ν, cm^{-1}: 1640, 1470. ^1H NMR spectrum, δ, ppm: 5.55 s (2H, CH_2), 7.15–8.62 m (14H, CH= and H_{arom}), 11.34 s (1H, NH). UV spectrum (toluene), λ_{max}, nm ($\varepsilon \times 10^{-4}$ l mol^{-1} cm^{-1}): 296 (1.59), 317 (1.51), 353 (0.65), 372 (0.77), 438 (1.54). Found, %: C 78.22; H 4.81; N 3.75; S 8.61. $C_{24}H_{17}NOS$. Calculated, %: C 78.44; H 4.66; N 3.81; S 8.72.

2-[Acetyl(9-anthrylmethyl)aminomethylene]benzo[*b*]thiophene-3(2*H*)-one (II). Ketoenamine **I**, 0.26 g (0.7 mmol) was dissolved in 2 ml (0.021 mol) of acetic anhydride, 0.17 ml (1.2 mmol) of triethylamine was added, and the mixture was heated under reflux for 5 min. The solution was cooled, and the precipitate was filtered off and twice recrystallized from benzene. Yield 0.13 g (45%). Yellow powder with mp 203–204°C. IR spectrum, ν, cm^{-1}: 1680, 1560, 1470, 1380. ^1H NMR spectrum, δ, ppm: 2.22 s (3H, CH_3), 5.93 s (2H, CH_2). 7.20–8.45 m (14H, CH= and H_{arom}). UV spectrum (toluene), λ_{max}, nm ($\varepsilon \times 10^{-4}$ l mol^{-1} cm^{-1}): 301 (1.93), 338 (0.43), 354 (0.74), 372 (1.03), 397 (1.17), 428 (1.29). Found, %: C 76.41; H 4.55; N 3.40; S 7.80. $C_{26}H_{19}NO_2S$. Calculated, %: C 72.26; H 4.67; N 3.42; S 7.83.

The IR spectra were measured on a Specord 75IR spectrometer from samples dispersed in mineral oil. The ^1H NMR spectra were obtained on a Varian Unity 300 spectrometer (300 MHz) in $CDCl_3$ using TMS as external reference. The electron absorption spectra were recorded on a Specord M-40 spectrophotometer, and the fluorescence spectra were measured on a Hitachi spectrofluorimeter. Solutions of **I** and **II** were irradiated with a DRSh-250 mercury lamp using a set of replaceable light filters.

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