

SHORT
COMMUNICATIONS

2-[N-Acetyl-N-(2-fluorenyl)aminomethylene]benzo[b]thiophen-3(2H)-one, a Molecular Fluorescent Switch*

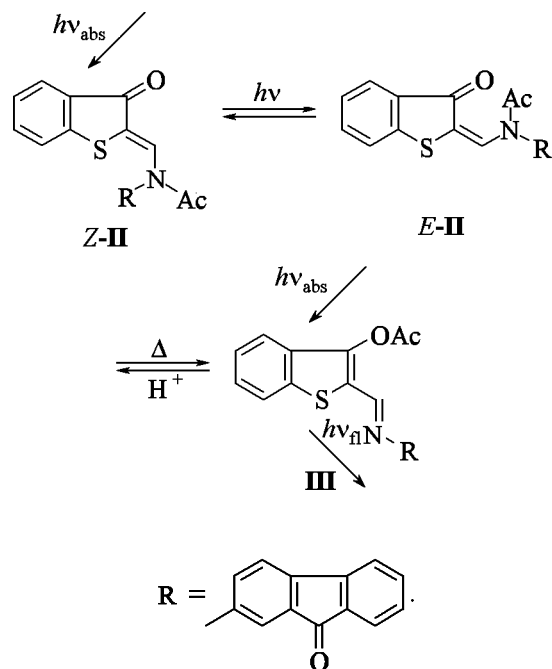
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Received July 17, 2002

Bistable molecular switches ensure transmittance and interruption of a light signal [1, 2], and a presence of a coordination site capable of fixing metal cations transforms them into photochromic chemosensors [3, 4]. Especially interesting are the systems where one of the stable forms has fluorescent properties [5, 6].

By acylation of 2-[N-(2-fluorenyl)aminomethylene]benzo[b]thiophen-3(2H)-one (**I**) we obtained



N-acylated ketoenamine **II** that represents a new type of light regulator of a fluorescent information signal based on photoinitiated reversible N→O acylotropic rearrangement.

According to the data of electronic, vibrational, and ^1H NMR spectroscopy compound **II** has Z-configuration at the C=C bond [4], possesses characteristic absorption band at 428 nm, and lacks fluorescence. The irradiation of its solution in acetonitrile with radiation close to the longwave maximum of the compound (λ_{exc} 436 nm) results in isomerization at the C=C bond followed by N→O migration of acetyl group ($\Phi_{\text{II} \rightarrow \text{III}}$ 0.18) and formation of the O-acylated isomer **III** possessing a strong absorption band at 350–380 nm and a fluorescence (λ_{max} 545 nm, η 0.03). Compound **III** is very stable at room temperature but thermal initiation or catalytic amounts of trifluoroacetic acid bring about its isomerization into initial ketoenamine **II**. This is the first known example of fluorescence excitation in the N→O process of acylotropic transfer for with the previously studied O-acylated structures of **III** type with N-aryl substituents the luminescence has not been observed due to the fast intercombination conversion [7].

2-[N-(2-Fluorenyl)aminomethylene]benzo[b]thiophen-3(2H)-one (I). To a solution of 0.46 g (2.6 mmol) of 3-hydroxybenzo[b]thiophene-2-carbaldehyde [8] in 3 ml of toluene was added a solution of 0.5 g (2.6 mmol) of 2-aminofluorenone in 3 ml of toluene, and the mixture was heated to boiling for 3–5 min. The separated precipitate was filtered off and recrystallized from toluene. Yield 61%, red crystals, mp 300–302°C. IR spectrum, cm^{-1} : 1720, 1640. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 7.25–7.35 m (2H arom), 7.50–7.65 m (5H arom), 7.70–7.80 m (4H arom), 8.30–8.40 br.d (1H, CH, J 12.0 Hz),

* The study was carried out under financial support of the Russian Foundation for Basic research (grants nos. 02-03-32527 and 00.15-97320) and of CRDF Foundation of the Ministry of Education of the Russian Federation (grant no. REC-004).

10.30–10.40 br.d (1H, NH). Found, %: C 74.12; H 3.57; N 3.85. $C_{22}H_{13}NO_2S$. Calculated, %: C 74.34; H 3.69; N 3.94.

2-[N-Acetyl-N-(2-fluorenonyl)aminomethylene]-benzo[b]thiophen-3(2H)-one (II). To 0.2 g (0.56 mmol) of ketoenamine **I** was added 5 ml (51.9 mmol) of acetic anhydride, and then 0.32 ml of triethylamine. The mixture was boiled for 10–15 min till compound **I** dissolved, then the solution was cooled, the separated precipitate was filtered off and recrystallized from toluene. Yield 67%, yellow crystals, mp 279–281°C. IR spectrum, cm^{-1} : 1720, 1690, 1670. 1H NMR spectrum ($CDCl_3$), δ , ppm: 2.00–2.30 br.s (3H, CH_3), 7.10–7.30 m (2H arom), 7.35–7.45 m (3H arom), 7.55–7.90 m (6H arom), 8.70–8.90 br.s (1H, CH). UV spectrum, λ_{max} , nm ($\epsilon \cdot 10^{-4} \text{ j} \cdot cm^{-1} \cdot mol^{-1}$): 310 (2.96), 428 (1.29). Found, %: C 72.31; H 3.78; N 3.11. $C_{24}H_{15}NO_3S$. Calculated, %: C 72.52; H 3.80; N 3.52.

IR spectra were recorded from mulls in mineral oil on spectrophotometer Specord 75IR. 1H NMR spectra were registered on spectrometer Varian Unity 300 (300 MHz), reference TMS. Electron absorption spectra in acetonitrile were measured on Specord M-40 instrument, emission spectra were registered on spectrofluorimeter "Elumin". The solution of com-

pound **II** in acetonitrile was irradiated with mercury lamp DRSh-250 equipped with a set of changeable filters.

REFERENCES

1. Minkin, V.I., *Ros. Khim. Zh.*, 2000, vol. 44, no. 6, p. 3.
2. Feringa, B.L., van Delden, R.A., Koumura, N., and Geertsema, E.M., *Chem. Rev.*, 2000, vol. 100, no. 5, p. 1789.
3. Bren', V.A., *Usp. Khim.*, 2001, vol. 70, no. 12, pp. 1152.
4. Rybalkin, V.P., Popova, L.L., Dubonosov, A.D., Shepelenko, E.N., Revinskii, Yu.V., Bren', V.A., and Minkin, V.I., *Zh. Org. Khim.*, 2001, vol. 37, no. 9, p. 1384.
5. De Silva, A.P., Fox, D.B., Moody, T.S., and Weir, S.M., *Trends in Biotechnology*, 2001, vol. 19, no. 1, p. 29.
6. Fernandez-Acebes, A. and Lehn, J.-M., *Chem. Eur. J.*, 1999, vol. 5, no. 11, p. 3285.
7. Knyazhanskii, M.I., Lyubarskaya, A.E., and Palui, G.D., *Khim. Vys. Energii*, 1980, vol. 14, no. 2, p. 130.
8. Bren', V.A., Usacheva, V.I., and Minkin, V.I., *Khim. Geterotsykl. Soed.*, 1972, no. 7, p. 920.