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SYNTHESIS AND SPECTRAL-LUMINISCENCE PROPERTIES OF A SYMMETRICAL SQUARAINE – A BENZOXAZOLIUM DERIVATIVE

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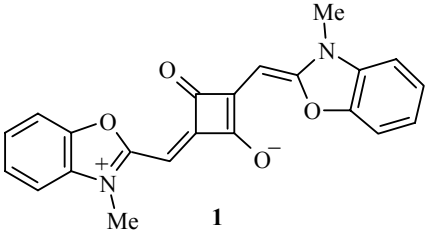
The major approach for the preparation of squarilium dyes, which have a number of important technical applications involving the transformation of light energy [1], is still the condensation of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) with methyl-substituted heterocyclic onium salts [2]. Although this pathway, which was proposed more than 40 years ago by Sprenger and Ziegenbein [3], has led to the synthesis of many such dyes [2, 3], it has been impossible to prepare symmetrical squarilium dyes with 1,3-benzoxazolium fragment [4]. Only asymmetrical squaraines with a single benzoxazolium moiety have been synthesized [4]. Since oxapentamethinecyanine has strong fluorescence (the fluorescence quantum yield is 49% in ethanol [5]), it was of interest to synthesize a symmetrical benzoxazolium squarilium dye and study its spectroluminescent properties. We unsuccessfully attempted to prepare this compound using a classical approach by the azeotropic distillation of water from a mixture of 1-butanol and toluene and pyridine or quinoline as the base. In contrast, carrying out this reaction in 2:1 1-pentanol–chlorobenzene and, quite significantly, with the use of a stronger and more sterically hindered base, namely, diisopropylethylamine, permitted the condensation of 2,3-dimethylbenzoxazolium *p*-toluenesulfonate with squaric acid to give a symmetrical squarilium dye **1** in yields up to 6%.



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The long-wavelength absorption (λ^a) and fluorescence (λ^f) bands for dye **1** are as follows: $\lambda^a_{max,}$ nm ($\varepsilon \cdot 10^{-4}$) = 573 (25.68) in EtOH, 592 (23.39) in DMF, and 586 (23.00) in $CHCl_3$ and λ^f_{max}, nm (Φ, %) = 584 (11) in EtOH, 604 (13) in DMF, and 596 (43) in $CHCl_3$.

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Hence, dye **1** absorbs approximately in the same region and with the same intensity as 3,3'-diethyloxadicarbocyanine (DODC) (λ^a_{max} ($\varepsilon \cdot 10^{-4}$) = 582 nm (23.8) and λ^f_{max} (Φ, %) = 610 nm (49) in ethanol [5]). The fluoresence Stokes shift of dye **1** is less than for DODC. The fluorescence quantum yield increases with decreasing polarity of the solvent.

The ^{1}H NMR spectra were taken on a Varian VXR-300 spectrometer at 300 MHz in deuterochloroform with TMS as the internal standard. The electronic absorption spectra were taken on a Shimadzu UV-3100 spectrophotometer. The fluorescence spectra were taken on a SOLAR SM 2203 spectrofluorimeter manufactured in Belarus. The fluorescence quantum yield of the dye was measured relative to the fluorescence quantum yield of indodicarbocyanine in ethanol (Φ = 28% [6]). The optical density of the solutions at the excitation wavelength did not exceed 0.1. A correction was introduced in determining the quantum yield in chloroform and DMF accounting for the change in the solvent refraction index. The purity of the compounds was monitored by thin-layer chromatography on Silufol UV-254 plates.

(4*E*)-4-[(3-Methyl-1,3-benzoxazol-3-io-2-yl)methylene]-2-[(*E*)-(3-methyl-1,3-benzoxazol-2(3H)-ylidene)-methyl]-3-oxo-1-cyclobuten-1-olate (1). A mixture of 2,3-dimethyl-1,3-benzoxazolium *p*-toluenesulfonate (3.50 g, 11 mmol), squaric acid (0.57 g, 5 mmol), and diisopropylethylamine (1.42 g, 11 mmol) in a mixture of 1-pentanol (40 ml) and chlorobenzene (20 ml) was heated with the azeotropic distillation of water for 8 h. The solvent was removed in vacuum. The residue was subjected to chromatography on alumina with 7:1 acetonitrile–ethanol as the eluent. The fraction containing the dye was evaporated under reduced pressure and resubjected to chromatography with 9:1 acetonitrile–ethanol as the eluent. After removal of the solvent, the residue was dissolved in chloroform and filtered. Chloroform was removed in vacuum. The dye was crystallized from 2:1 acetonitrile–ethanol. The yield of **1** was 0.111 g (6%); mp 248-250°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.58 (6H, s, NCH_3); 5.36 (2H, s, =CH); 7.08 (2H, dd, ^3J = 8.1, ^4J = 1.2, Ar–H); 7.22 (2H, td, ^3J = 8.1, ^4J = 1.2, Ar–H); 7.29 (2H, t, J = 8.1, Ar–H); 7.55 (2H, d, J = 8.1, Ar–H). Found, %: C 70.66; H 4.25; N 7.47. $C_{22}H_{16}N_2O_4$. Calculated, %: C 70.96; H 4.33; N 7.52.

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