α-PYRYLOTETRACARBOCYANINES

M. A. Kudinova, Yu. L. Slominskii, and A. I. Tolmachev

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The synthesis of polymethine dyes having the greatest possible long-wavelength absorption and the simplest possible structure is an urgent problem, since dyes are more stable than are the compounds with a longer polymethine chain that absorb in the same region. Bridging groups in the polymethine chain of polycarbocyanines also increase their stability [1], allowing us to synthesize dyes IIIa-e, which are the first members of the α series of pyrylotetracarbocyanines, by condensing pyrylium salts and their thio and seleno analogs (Ia-e) with derivatives of 2,4-heptadiene-1,7-dial (II).

I, III a.c., e $R^1-R^2=-(CH_2)_2-$; b $R^1=R^2=H$; d $R^1-R^2=-(CH_2)_3-$; a X=O; b-d X=S; e X=Se

The structure of these dyes is confirmed by the intense absorption in the 1100-1280-nm region. Dyes IIIa-e absorb at wavelengths ~ 100 nm longer than their isomers in the γ series [1], and thus selenopyrylotetracarbocyanine IIIe absorbs at the longest wavelengths among all the presently known dyes with the same length of the polymethine chain. Despite this fact, a solution of dye IIIe (in CH₂Cl₂, c = $4 \cdot 10^{-6}$ M) remained unchanged after storage in the dark at room temperature for 1 month. The following are the yield (%) and $\lambda_{\rm max}$ (nm) (log ϵ) (CH₂Cl₂) for the dyes of type III: IIIa 17, 1040, 1180 (4.97, 5.32); IIIb 25, 1076, 1223 (4.96, 5.12); IIIc 66, 1270 (5.13); IIId 17, 1220 (4.59); IIIe 20, 1280 (5.23).

The data from the elemental analysis correspond to the calculated values.

LITERATURE CITED

1. Yu. L. Slominskii, A. L. Smirnova, M. A. Kudinova, N. I. Efimenko, and A. I. Tolmachev, Ukr. Khim. Zh., 43, 838 (1978).

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