SYNTHESIS OF TETRA- AND PENTACARBOCYANINE DYES WITH ALKOXY GROUPS IN THE β, β' POSITIONS OF THE POLYMETHINE CHAIN

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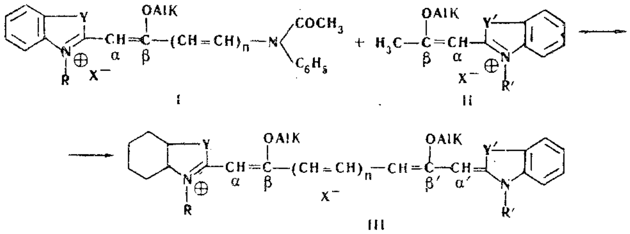
Previously unknown symmetrical and unsymmetrical β, β'-dialkoxytetracarbocyanine and β, β'-dialkoxypentacarbocyanine dyes have been synthesized by the condensation of β-alkoxy-substituted hexamethine and octamethine hemicyanines with quaternary salts of β-alkoxypropenyl derivatives of heterocyclic bases. Tetracarbocyanines with a symmetrical structure have also been obtained by the direct interaction of quaternary salts of β-alkoxypropenyl derivatives of heterocyclic bases with malonaldehyde dianil.

It has previously been shown that the condensation of β-alkoxy-substituted tetramethine hemicyanine dyes (I; n = 1) with quaternary salts of β-alkoxypropenyl derivatives of heterocyclic bases (II) readily forms symmetrical and unsymmetrical tricarbocyanines containing alkoxy groups in the β, β' positions of the polymethine chain (III; n = 1) [1, 2].



We have recently synthesized higher vinylene homologs of I (n = 1, 2) [2, 3]. In connection with this, it appeared of interest to attempt to carry out the condensation of the hexamethine and octamethine hemicyanines so obtained with the salts II, which might be expected to form the previously unknown β, β'-dialkoxy-substituted tetracarbocyanine and pentacarbocyanine dyes III (n = = 2, 3). When triethylamine was added to a mixture of the ethiodide of 2-β-ethoxy-ω-acetanilidohexatrienylbenzothiazole (IV) and the ethyl ethosulfate of 2-β-ethoxypropenylbenzothiazole (V) in anhydrous ethanol, an intense blue-green coloration immediately appeared and golden crystals rapidly began to separate. The dye obtained was found to be 3, 3'-diethyl-9, 15-diethoxythiatetracarbocyanine iodide (III; Y = Y' = S; R = R' = Alk = = C_2H_5; X = I; n = 2). Similarly, 2-β-ethoxy-ω-acetanilidooctatetraenyl-benzothiazole and V, on being heated for 5 min in boiling ethanol in the presence of triethylamine, gave 3, 3'-diethyl-9, 17-diethoxythiapentacarbocyanine iodide (III, Y = Y' = S; R = R' = Alk = C_2H_5; X = I; n = 3). In this way, a series of symmetrical and unsymmetrical thia- and selenatetracarbocyanine and pentacarbocyanine dyes was obtained [3]. It was found that the symmetrical tetracarbocyanines (III, n = = 2) can also be synthesized, although in low yields, by the direct interaction of 2 moles of the propenyl salt with 1 mole of malonaldehyde dianil in acetic anhydride in the presence of triethylamine at 15°–20° C [4]. The absorption maxima of the dyes III are displaced to the short-wave region in comparison with those of compounds unsubstituted in the polymethine chain, as in other cases [5, 6]. The β, β'-dialkoxytetra- and -pentacarbocyanines exhibit a greater sensitizing action than dyes not containing alkoxy groups. However, they sensitize silver halide emulsions to shorter rays.

EXPERIMENTAL

3, 3'-Diethyl-9, 15-diethoxythiatetracarbocyanine iodide. a) To 0.55 g (0.001 mole) of IV and 0.38 g (0.001 mole) of V in 10 ml of anhydrous ethanol was added 0.15 g (0.0015 mole) of triethylamine (TEA), whereupon an intense blue-green coloration appeared and golden green crystals gradually deposited. After 20 hr, the precipitate was filtered off and washed with water, ethanol, and ether. Yield 0.55 g (84.5%), mp 155°–156° C.

b) A mixture of 0.76 g (0.002 mole) of V, 0.22 g (0.001 mole) of malonaldehyde dianil, 2 ml of acetic anhydride, and 0.2 g (0.002 mole) of TEA was left for 20 hr at 20°–25° C and was then diluted with ether. The precipitate that deposited was washed with ether and dissolved in 130 ml of ethanol, and an equal volume of a 10% aqueous solution of potassium iodide was added. The yield was 0.28 g (42%), mp 166°–168° C. For purification, the dye was crystallized from ethanol. Green prisms with a bronze tinge, mp 171°–172° C (decomp); λ_{max} 780 nm (here and below, λ_{max} is given in ethanol). Found, %: I 18.25. Calculated for $C_{31}H_{35}IN_2O_2S_2 \cdot C_2H_5OH$, %: I 18.02. **Perchlorate**: golden green prisms (from ethanol) mp 186°–187° C. Found, %: Cl 5.62. Calculated for $C_{31}H_{35}ClN_2O_6S_2$, % Cl 5.66.

3, 3'-Diethyl-9, 15-dimethoxyselenatetracarbocyanine iodide. Obtained in a similar manner to the preceding case (a), from 0.29 g (0.0005 mole) of 2-β-methoxy-ω-acetanilidohexatrienylbenzoselenazole ethiodide and 0.20 g (0.0005 mole) of the ethyl methyl sulfate derivative of 2-β-methoxypropenylbenzoselenazole (VI) in 5 ml of anhydrous ethanol in the presence of 0.1 g (0.001 mole) of TEA. Yield 0.20 g (55%), mp 144°–145° C; b) from 0.40 g (0.001 mole) of VI, 0.11 g (0.0005 mole) of malonaldehyde dianil, and 0.2 g (0.002 mole) of TEA in 2.0 ml of acetic anhydride. Yield 0.10 g (28%), mp 144°–145° C. Golden green prisms with mp 145°–146° C (after two washings with boiling ethanol); λ_{max} 790 nm. Found, %: I 17.35. Calculated for $C_{29}H_3IN_2O_2Se_2$, %; I 17.52.

3, 3'-Diethyl-9-ethoxy-15-methoxythiaselenatetracarbocyanine iodide. A mixture of 0.27 g (0.0005 mole) of IV, 0.20 g (0.0005 mole) of VI, 6 ml of anhydrous ethanol, and 0.1 g (0.001 mole) of TEA was heated in the boiling water bath for 2 minutes. After 20 hr, the crystalline precipitate was filtered off. Yield 0.20 g (62%), mp 151°–152° C. Golden green plates with mp 152°–153° C (after washing with boiling ethanol); λ_{max} 785 nm. Found, %: I 18.15. Calculated for $C_{30}H_{33}IN_2O_2SSe$, %: I 18.36.

3, 3'-Diethyl-9, 17-diethoxythiapentacarbocyanine iodide. A mixture of 0.57 g (0.001 mole) of 2-β-ethoxy-ω-acetanilidooctatetraenylbenzothiazole ethiodide (VII), 0.38 g (0.001 mole) of V, 10 ml of ethanol, and 0.2 g (0.002 mole) of TEA was heated in the boiling water bath for 5 min. The crystalline precipitate that separated on cooling was filtered off and washed with water, ethanol, and ether.

Yield 0.32 g (48%), mp 131°–133° C. Golden green needles, mp 145°–146° C (from methanol); λ_{max} 880 nm. Found, %: I 17. 92. Calculated for $C_{33}H_{37}IN_2O_2S_2 \cdot CH_3OH$, %: I 17.71. **Perchlorate:** golden green needles, mp 149°–150° C (from methanol). Found, %: Cl 5.66. Calculated for $C_{33}H_{37}ClN_2O_6S_2$, %: Cl 5.40.

3, 3'-Diethyl-9, 17-dimethoxyselenapentacarbocyanine iodide. Obtained similarly to the preceding compound from 0.30 g (0.0005 mole) of 2-β-methoxy-ω-acetanilidooctatetraenylbenzoselenazole and 0.20 g (0.0005 mole) of VI in 7 ml of ethanol in the presence of 0.1 g (0.001 mole) of TEA. Yield 0.15 g (40%). Dark green prisms with mp 151°–152° C; λ_{max} 890 nm. Found, %: I 16.70. Calculated for $C_{31}H_{33}IN_2O_2Se_2$, %: I 16.91.

3, 3'-Diethyl-9-ethoxy-17-methoxythiaselenapentacarbocyanine iodide. From 0.28 g (0.0005 mole) of VII and 0.20 g (0.0005 mole) of VI in 10 ml of ethanol in the presence of 0.1 g (0.001 mole) of TEA. Yield 0.17 g (49%). Golden green needles with mp 131°–132° C; λ_{max} 885 nm. Found, %: I 17.40. Calculated for $C_{32}H_{35}IN_2O_2SSe$, %: I 17.69.

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