SYNTHESIS OF A THIACARBOCYANINE WITHOUT ALKYL GROUPS ATTACHED TO THE NITROGEN ATOMS OF THE BENZOTHIAZOLE RINGS (NORTHIACARBOCYANINE)

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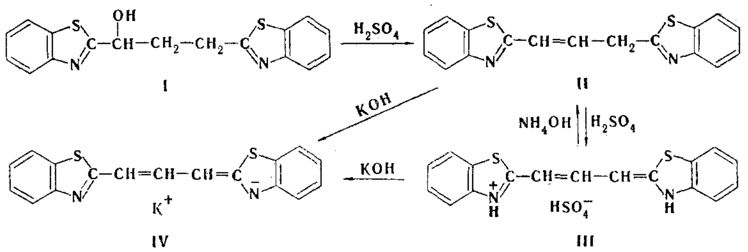
Thiacyanine dyes contain alkyl groups attached to the nitrogen atoms of the benzothiazole rings. Northiacarbocyanines have not been described. We have synthesized the simplest northiacarbocyanine (III) by dehydration of 1-hydroxy-1,3-di(2-benzothiazolyl)propane (I), obtained by condensation of α-hydroxyglutaric acid with o-aminothiophenol.



Compound I is converted to northiacarbocyanine (III), probably through a step involving the formation of 1,3-di(2-benzothiazolyl)-1-propane (II), on reaction with sulfuric acid. Compound III undergoes no changes when it is stored for a long time without access to moisture; it is decomposed by warm water, alcohol, and proton-acceptor solvents but is extremely stable in chloroform solution. The curve of the light absorption of dye III in alcohol solution in the presence of mineral acid has the form of the typical absorption curves of known thiacarbocyanines; the chief absorption maximum is at 548 nm. When an alcoholic KOH solution is added to an alcohol solution of dye III, one observes decolorization with the subsequent appearance, in the presence of excess alkali, of a new color (λ_{max} 536 nm) arising as a result of the formation of a polymethine dye anion (IV – the potassium salt of 1,3-di(2-benzothiazolyl)-1-propene. A yellowish precipitate, apparently tautomeric base II, is formed on treatment of an aqueous suspension of II with ammonium hydroxide; II was not isolated in the pure state, but it was shown that an alcohol solution of it becomes red from the addition of both hydrochloric acid and alkali solution, and the acid and alkaline solutions contain dyes with light absorption maxima at 548 and 536 nm, respectively.

EXPERIMENTAL

1-Hydroxy-1,3-di(2-benzothiazolyl)propane (I). A mixture of 11.1 g (0.075 mole) of α-hydroxyglutaric acid [1] and 17 g (0.136 mole) of o-aminothiophenol was heated at 160° for 10 h in a sealed glass tube to give 14 g (63.8%) of colorless crystals of I with mp 143-145° [from toluene–heptane (1 : 2.5)]. Found,%: N 8.5; S 19.5. $C_{17}H_{14}N_2OS_2$. Calculated,%: N 8.6; S 19.6.

2,3-(2-Benzothiazolinylidene)-1-propenyl-1-benzothiazolium Bisulfate (III, Northiacarbocyanine). A 1.63-g (0.005 mole) sample of I was stirred with 5.5 ml [10.1 g (0.105 mole)] of concentrated H_2SO_4 until all of the solid had dissolved. The solution was heated at 190-200° for 7 min, cooled, and poured over 50 g of ice. The precipitate was washed with water (+20°), dried in a vacuum desiccator, extracted with hot benzene, and washed with benzene. Found,%: N 7.1; S 23.2. $C_{17}H_{14}N_2O_4S_3$. Calculated,%: N 6.9; S 23.7.

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LITERATURE CITED

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