SYMMETRICAL DYES — DERIVATIVES OF NAPHTHO[1,8-b,c]THIOPHENE

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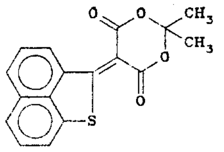
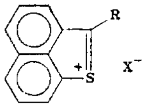
Only the unsymmetrical cationic dyes, in which the positive charge is localized at the nitrogen atom of the second nucleus, are known for the peri-condensed naphtho[1,8-b,c]thiophene system [1, 2].

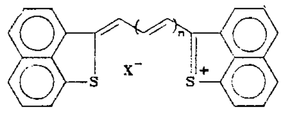
We obtained the 2-methylnaphthothiolium salt (IIa) by the decomposition of the dye (I) [3] with p-toluenesulfonic acid. The condensation of (IIa) with the salt (IIb) [3] in the mixture of acetic anhydride and p-toluenesulfonic acid gave the dye (III), which was converted to the perchlorate (n = 0, X = ClO_4^-).



I



II



III

IIa R=CH_3, X=p-$CH_3C_6H_4SO_3$; b R=SCH_3, X=CH_3OSO_3

The narrow well-resolved absorption curve of this dye (λ_{max} 678 nm, log ε 15.5, nitromethane) indicates the absence of steric hindrance in the molecule; the hindrance would be possible in the single favorable conformation with the sulfur atoms drawn together.

When the salt (IIa) is treated with orthoformic ester or 1,1,3,3-tetraethoxypropane, the dyes (III) (n = 1, 2) are formed judging from the absorption maxima ($_{max}$ 850 and 930 nm, nitromethane); (III) could not be isolated in the pure form.

Considering the first vinylene shift, which equals 172 nm, it seems that this is explained by the interaction of the sulfur atoms drawn together in the di-cis-conformation, as is also the case for some other sulfur-containing monomethinecyanines [4, 5].

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