

## A MACROCYCLIC BIS-CYANINE DYE

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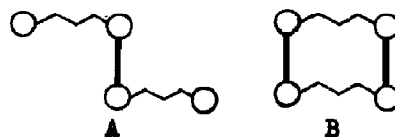
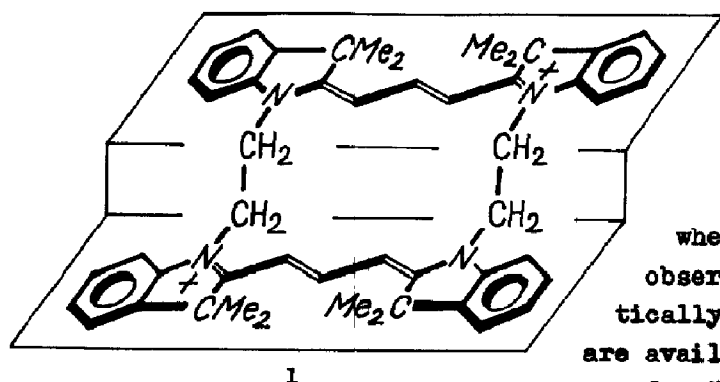
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**Abstract.** - The bis-indocarbocyanine 1, the first dye of a "sandwich" type with parallel polymethine chains bonded by two ethylene links, is described. Its structure is proved with the help of visible spectra based upon the theory of chromophore interaction.

The phenomenon of intramolecular chromophore interaction was observed in the visible spectra of bis-cyanine dyes and first correctly explained by A.I.Kiprianov and one of us (I.L.M.) in 1965 [1]. Since then many examples illustrating this phenomenon has become available. Among them there are bis-dyes with conjugated chromophores (for a review see [2]), bis-cyanines with non-conjugated chromophores [3], as well as colourless compounds having a similar structure [4]. But no-one has yet synthesized a bis-dye with a zero  $\varphi$  angle between the directions of the polymethine chromophores. Such a compound would be interesting in that its most intense absorption band is expected to be shifted to shorter wavelengths in comparison with the corresponding monochromophore dye band [5]. We present here the first example of such dyes with  $\varphi = 0$ , the bis-indocarbocyanine 1. Its visible spectrum, treated in terms of the theory of chromophore interaction, provides the simplest and most unambiguous demonstration of its structure.



Almost all known bis-compounds where chromophore interaction is observed can be represented schematically by formula A. Much fewer data are available about their cyclic analogues of a "sandwich" type (formula B) [6]

to which 1 belongs. In fact the structure of a bis-dye with a zero  $\varphi$  angle between chromophores could be realized only in dyes of type B, not in A where the two non-bonded ends of the chromophores would repel (cf. dye 4).

1 was synthesized by the usual cyanine condensation method from the quaternary salt 2 [7]. The highest yield of 1, 6-7 per cent, was obtained when 0.445 g of salt 2 was heated with 0.3 g of ethyl orthoformate in 2 ml of acetic anhydride - pyridine (1:1) mixture at 130° for 5 minutes. The yield of di-

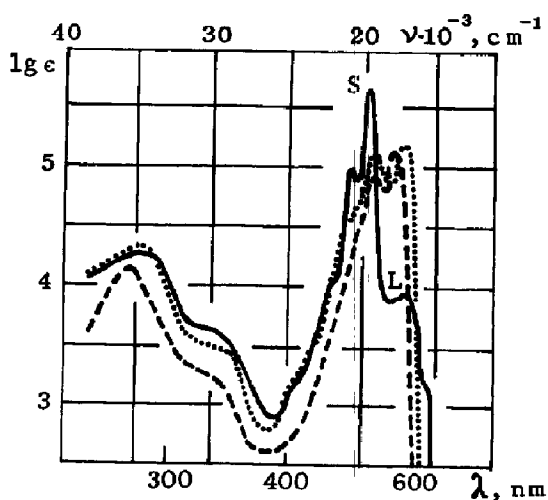
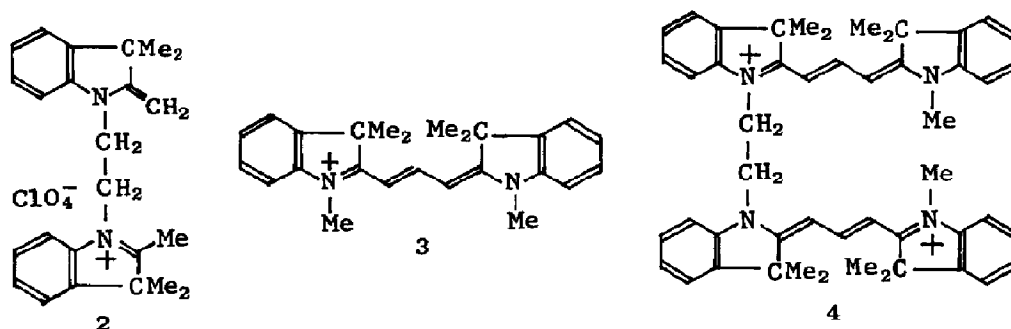


Figure 1. Absorption spectra (in  $\text{CH}_2\text{Cl}_2$ ). Full curve - 1, broken curve - 3, dotted curve - 4.

perchlorate 1,  $\text{C}_{50}\text{H}_{54}\text{Cl}_2\text{N}_4\text{O}_8$ , is low, but the analytically pure product crystallises from the reaction mixture. Small prisms of 1 decompose at above 300°. Its solutions have a pale reddish orange colour due to the extreme narrowness of the principal band S (figure 1) in the spectrum at 506 nm ( $\lg \epsilon$  5.68). This band is shifted to shorter wavelengths in comparison with the monochromophore dye 3 absorption band,  $\lambda_{\text{max}}$  550 nm ( $\lg \epsilon$  5.15). It indicates that 1 has a zero  $\varphi$  angle between two polymethine chromophores. Another band (L) at 590 nm of a 50 times lower intensity ( $\lg \epsilon$  3.98) is also observed in the spectrum of 1. Its origin will be discussed below.

For comparison we also synthesized the bis-indocarbocyanine 4 of type A. A mixture of 0.445 g of salt 2 and 0.402 g of 1,3,3-trimethyl-2-formylmethyleneindoline was boiled with 6 ml of acetic anhydride for 3 minutes. The dye was precipitated by ether and converted into diperchlorate,  $\text{C}_{50}\text{H}_{56}\text{Cl}_2\text{N}_4\text{O}_8$ ,



yield 88 per cent, m.p. 280–282° (decomp.). Its spectrum is presented in figure 1. Two bands with  $\lambda_{\text{max}}$  509 and 572 nm and nearly the same intensity (lg  $\epsilon$  5.21 and 5.29 respectively) show that the  $\varphi$  angle is far from zero.

1 undergoes a reversible protonation in concentrated sulfuric acid to form a colourless tetracation (cf. [8]). But in a ~ 50 per cent  $\text{H}_2\text{SO}_4$  an intense purple colour develops and an absorption band at 560 nm occurs in the spectrum. Its shape and location are typical of indocarbocyanine dyes and prove that a trication with one trimethine chromophore is formed. These conversions support the bis-trimethine structure 1.

A solution of 1 in  $\text{CH}_2\text{Cl}_2$  shows a deep red luminescence with its maximum at 662 nm. The excitation spectrum of this emission was found to coincide with the absorption spectrum. This fact unambiguously shows that the band at 506 and that at 590 nm belong to the same substance. The extremely large Stokes shift ( $\Delta\nu = 4660 \text{ cm}^{-1}$ ) may suggest that phosphorescence occurs, but it is not quenched by anthracene, which has a triplet state at  $14900 \text{ cm}^{-1}$  (670 nm), i.e. near the resonance with the expected triplet of 1. Failing phosphorescence, it is then fluorescence that takes place. Thus, the absence of the O–O transition both in the absorption and fluorescence spectra suggest the strongly forbidden character of the long wavelength band, i.e. a zero  $\varphi$  angle in dication 1.

The inspection of the molecular models of dication 1 shows that, unlike dyes of type B whose chromophores are bonded with the odd number of methylene groups (cf. [6]), it can exist in three fixed conformations similar to those of cyclohexane [9]: the chair, C (the symmetry group  $\text{C}_{2h}$ ), the twisted boat, TB ( $\text{D}_2$ ), and the boat, B ( $\text{C}_{2v}$ ). B is strongly hindered in the case of 1, so its fraction is negligible. C seems preferable to TB because of a smaller hindrance between the meso-hydrogen atoms in each of the polymethine chains. The angle between the directions of two trimethine chromophores in C is precisely zero and is 28° in the TB case [10]. The absorption band at 590 nm could be assigned either to C or to TB but the fluorescence experiments mentioned above prove the predominance of the centrosymmetrical C [11] with a zero  $\varphi$  angle between chromophores.

## REFERENCES AND NOTES

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5. Chromophore interaction consists in splitting the energy level which corresponds to a monochromophore dye that gives rise in an electron spectrum of a bis-dye to two bands. The intensity of the long wavelength band is zero when the angle between the chromophore directions is zero. See A.I.Kiprianov, G.G.Dyadyusha. Ukr.Khim.Zh., 35, 608 (1969).
6. A synthesis scheme for similar bis-thiacarbocyanine dyes with the  $-(CH_2)_n-$  groupings between quaternary nitrogen atoms is mentioned by D.M.Sturmer in "Special Topics in Heterocyclic Chemistry", Ed. A.Weissberger and E.C.Taylor, John Wiley & Sons, New York etc, 1977, p. 514, without any indication of their properties. The visible spectrum of the dye with  $-(CH_2)_5-$  bridges is reproduced by A.H.Herz in Photogr. Science and Eng., 18, 327 (1974).
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8. A.I.Tolmachev, M.Yu.Kornilov, E.F.Karaban. Teor.Eksp.Khim., 12, 817 (1976); S.G.Fridman, A.I.Kiprianov. Zh.Org.Khim., 4, 696 (1968).
9. We assume the rigid and all-trans structure of both monochromophores.
10. The figure was obtained on Dreiding model of 1.
11. The 590 nm band is interpreted here as a vibronic transition of the forbidden long wavelength band. This transition is permitted by a combination with an antisymmetrical vibration mode, with borrowing of intensity from the short wavelength band.

(Received in UK 27 March 1980)