

PYRYLOCYANINES

III.* UNSYMMETRICAL SELENAFLAVYLOCYANINES

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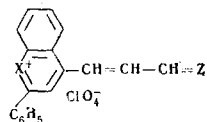
Unsymmetrical selenafavylocyanines containing flavylum, thiaflavylium, 1,3,3-trimethyl-indoleninium, or 1-ethylbenzothiazolium rings were synthesized. The deviations for the dyes obtained, which were calculated from the absorption maxima and by the "band moment" method, were compared with the same values obtained for similar dyes with flavylum or thiaflavylium rings in place of the selenafavylium ring. The results indicate that the basicity of the heterorings in the polymethine dyes increases in the order selenafavylium < thiaflavylium < flavylum. This is confirmed by a comparison of the deviations in hemicyanines and styryls.

In our previous communication [1] we described symmetrical selenafavylocyanines, which proved to be the most deeply colored dyes of the polymethine dyes of the same chromophore length. In the present study we have obtained a number of unsymmetrical selenafavylocyanines in order to determine the relative basicity of the selenafavylium ring. As in the preparation of symmetrical selenafavylocyanines, the starting compounds for the synthesis were 4-methyl- and 4-methoxyselenafavylium salts (I-II), as well as 4-(ω -anilinovinyl)selenafavylium perchlorate (IIIc), which was obtained by the condensation of salt I with ethylisoformanilide (see scheme on next page).

(Selenafavylo)(flavylo)- and (selenafavylo)(thiaflavylo)trimethylidenecyanines (V and VI) (see Table 1), respectively, were obtained by the reaction of hemicyanine IIIc with 4-methylflavylium and 4-methylthiaflavylium perchlorates. (Selenafavylo)(indo)- and (selenafavylo)(thia)trimethylidenecyanines (IX and XII), respectively, were obtained by the reaction of I with 1,3,3-trimethyl-2-formylmethyleneindoline and 1-ethyl-2-(ω -acetanilidovinyl)benzothiazolium iodide.) The oxygen analogs (VII and X) were synthesized in order to make a comparison of the absorption spectra.

* See [1] for communication II.

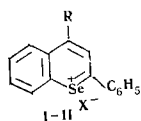
TABLE 1.



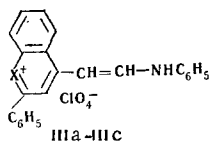
Comp	X	Z	λ_{max} , nm in CH ₃ NO ₂	M ⁻¹ , nm	D, nm	D _M , nm
IV	S	2-Phenyl-4-benzopyranylidene	750	726,0	2	2,4
V	Se	2-Phenyl-4-benzopyranylidene	770	736,9	1,5	8,6
VI	Se	2-Phenyl-4-benzothiaopyranylidene	810	773,1	5,5	11,7
VII	O	1,3,3-Trimethyl-2-indolinylidene	588	569,8	38,5	36,7
VIII	S	"	618	597,5	51,5	48,4
IX	Se	"	606	591,1	84	71,8
X	O	3-Ethyl-2-benzothiazolinyldene	569	547,8	64	66,3
XI	S	"	590	576,9	87	76,6
XII	Se	"	574	562,9	122,5	107,6

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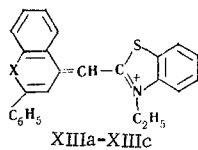


I R=CH₃, X=ClO₄;
 II R=OCH₃, X=o-NOC₆H₄SO₃;

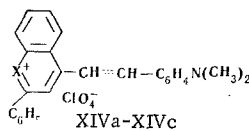


IIIa X=O, λ_{max} 492nm, D 6 nm
 IIIb X=S, λ_{max} 530nm, D 16 nm
 IIIc X=Se, λ_{max} 546nm, D 22 nm

In addition to the trimethylidenecyanines, a monomethylidenecyanine (XIIIc) was obtained by the condensation of salt I with 1-ethyl-2-sulfobenzothiazolium betaine, and a styryl (XIVc) was obtained from salt I and p-dimethylaminobenzaldehyde.



XIIIa X=O, λ_{max} 482 nm, D 30,5 nm
 XIIIb X=S, λ_{max} 514 nm, D 45 nm
 XIIIc X=Se, λ_{max} 516 nm, D 67,5 nm



XIVa X=O, λ_{max} 684 nm, M⁻¹ 657,3 nm
 D 26 nm, D_M 17,7 nm
 XIVb X=S, λ_{max} 725 nm, M⁻¹ 695,6 nm,
 D 23 nm, D_M 16,6 nm
 XIVc X=Se, λ_{max} 748 nm, M⁻¹ 708,8 nm,
 D 26,5 nm, D_M 12,8 nm

The electronic absorption spectra of nitromethane solutions of symmetrical selenaflylotrimethylidenecyanine (XIII) (curve 1) and (selenaflylo)(thia)trimethylidenecyanine (XII) (curve 2) are presented in Fig. 1. As seen from Fig. 1, in contrast to absorption curve 1, which has the shape typical for polymethine dyes, curve 2 falls obliquely into both the short-wave and long-wave regions. It can be assumed that still another low-intensity maximum is hidden in the long-wave region. In fact, two distinctly expressed maxima (with the long-wave maximum of lower intensity) are observed for different unsymmetrical dyes, for example, (flavylo)(indo)trimethylidenecyanine (VII) (curve 3). As in the case of several other cyanine dyes [2], the ratio of the intensities of these maxima is independent of the concentration, which repudiates the explanation of one of the bands by the aggregated state of the dye. In the case of dye VII, it has been shown that the difference in the frequencies ($\Delta\nu$) between both bands, as for symmetrical cyanines [3], is independent of the nature of the solvent. (It is the same in nitromethane, chloroform, and nitrobenzene.) In addition, like polymethine dyes for which the long-wave maximum (the "α band") is more intense than the short-wave band (the "β band"), $\Delta\nu$ for compounds of the VII type is about 1200 cm⁻¹. This value is ascribed to the completely symmetrical vibrations of the carbon atoms of the conjugation chain in the excited state [4]. Thus it should be concluded that in dyes of the VII type both long-wave maxima apparently are affiliated with the same electronic transition.

A method involving calculation of the deviations (D) – the deviations of the absorption maxima of the unsymmetrical dye from the arithmetic mean of the maxima of the two symmetrical dyes [5] – is usually employed to determine the relative basicity of the heterocyclic rings of which the dye is composed. Because the curves of the symmetrical and unsymmetrical dyes have different shapes and a fine structure is displayed in the case under consideration, there may be some doubt that it can be precisely taken as the absorption maximum. In addition to calculation of the deviations from the more intense absorption maxima

(D), we therefore also employed the determination of the deviations from the average positions of the absorption bands, which is determined by the ratio of the zero and first moments [6] of these bands (D_M). This method has already been used for this purpose [7].

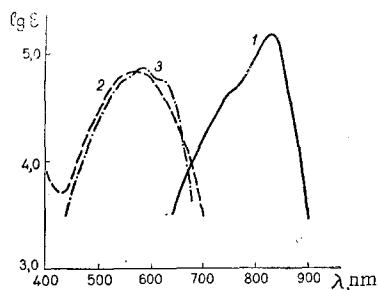


Fig. 1. UV spectra: 1) XIII; 2) XII; 3) VII.

The values of the most intense absorption maxima, the average positions of the absorption bands on the wavelength scale (M⁻¹) for nitromethane solutions, and the deviations obtained by the D and D_M methods are compared in Table 1 for unsymmetrical carbocyanines constructed from selenaflylium, flavylium, and thiaflavylium residues

[8]. The λ_{\max} and M^{-1} values for symmetrical flavyl-, thiaflavyl-, and selenaflavylcyanines were taken from [1] for the calculation of D and D_M , while the following values were obtained for symmetrical thia- and indocarbocyanines: λ_{\max} 558 and 545 nm, and M^{-1} 539.2 and 524.0 nm, respectively.

Both the D and D_M values are small for dyes IV-VI, which indicates the comparatively similar basicities of the flavylum, thiaflavylum, and selenaflavylum rings. More precise conclusions regarding their comparative basicities can be drawn from the deviations of VII-IX and X-XII. The deviations of both D and D_M for these dyes increase in the order $O < S < Se$. The D values for hemicyanines IIIa-IIIc and monomethylidenecyanines XIIIa-XIIIc change in the same order. The deviations of the hemicyanines were calculated according to [9] from the maxima of symmetrical monomethylidenecyanines [1,8] and malonic dialdehyde dianil hydrochloride (λ_{\max} 397 nm). It turned out that D and D_M have negative values for XIVc and its oxygen and sulfur analogs [8] XIVa and XIVb. It should be emphasized that the D_M value is minimally negative for the above-described dyes of different types, i.e., for styryl with a selenaflavylum ring, while the D value does not display this sort of regularity. The possibility of negative deviations was given a theoretical substantiation by Dyadyusha [10]. An example with styryls, as well as the reverse order of the change in D and D_M for IV and V during calculation of the deviations of the dyes from the complex absorption curve, demonstrate that the "band moment" method is more reliable.

Judging from the deviations in the polymethine dyes, the selenaflavylum ring is less basic than the thiaflavylum ring, which in turn is less basic than the flavylum ring, while it is known that the resistance of heteroaromatic cations to hydrolysis changes in the order $S > Se > O$ [11].

EXPERIMENTAL

4-(ω -Anilino)vinyl)selenaflavylum Perchlorate (IIIc). A mixture of 0.767 g (2 mmole) of I and 4 ml (2 mmole) of ethylisofromanilide [12] was heated at 50° for 1 h. The product was removed by filtration and purified by chromatography from chloroform with a column filled with aluminum oxide with subsequent precipitation of an alcohol solution with 20% perchloric acid and crystallization from glacial acetic acid to give 0.44 g (47%) of red crystals with mp 214° (dec.). Found %: Se 16.61. $C_{23}H_{18}ClNO_4Se$. Calculated %: Se 16.23.

(Selenaflavyl)(flavyl)trimethylidenecyanine Perchlorate (V). A mixture of 0.121 g (0.25 mmole) of IIIc, 0.090 g (0.28 mmole) of 4-methylflavylum perchlorate [13], and 0.02 g of anhydrous sodium acetate in acetic anhydride-acetic acid (1:1) was refluxed for 15 min. The dye was removed by filtration, washed with glacial acetic acid, and crystallized from nitromethane to give 0.147 g (94%) of crystals with mp 285° (dec.). Found %: Se 13.22. $C_{33}H_{23}ClO_5Se$. Calculated %: Se 12.87.

(Selenaflavyl)(thiaflavyl)trimethylidenecyanine Perchlorate (VI). This compound [0.144 g (89%)] was obtained like V from 0.121 g (0.25 mmole) of IIIc and 0.84 g (0.28 mmole) of 4-methylthiaflavylum perchlorate [8] and had mp 271° (dec.). Found %: 12.83. $C_{33}H_{23}ClO_4SSe$. Calculated %: Se 12.55.

(Flavyl)(1,3,3-trimethylindo)trimethylidenecyanine Perchlorate (VII). A mixture of 0.102 g (0.25 mmole) of 4-(ω -anilino)vinylflavylum perchlorate [14], 0.068 g (0.25 mole) of 1,2,3,3-tetramethylindolinium perchlorate, and 0.02 g of anhydrous sodium acetate was heated in 2 ml of acetic anhydride-glacial acetic acid (1:1) for 1 h at 100-110°. The solution was cooled, and several drops of 20% perchloric acid were added. The dye was removed by filtration and purified by chromatography from chloroform on aluminum oxide, reprecipitated from acetic anhydride by the addition of 20% perchloric acid, and recrystallized from glacial acetic acid to give a product with mp 233° (dec.). Found: Cl 7.01%. $C_{29}H_{26}ClNO_5$. Calculated: Cl 7.05%.

(Selenaflavyl)(1,3,3-trimethylindo)trimethylidenecyanine Perchlorate (IX). A mixture of 0.191 g (5 mmole) of I, 0.1 g (0.5 mmole) of 1,3,3-trimethyl-2-formylmethyleneindoline, and 0.04 g (0.5 mmole) of anhydrous sodium acetate was heated in 2 ml of acetic anhydride at 120° for 1.5 h. The dye was removed by filtration, washed with glacial acetic acid, and crystallized from glacial acetic acid to give 0.225 g (79%) of blue crystals with mp 237° (dec.). Found %: Se 13.96. $C_{29}H_{26}ClNO_4Se$. Calculated %: Se 13.94.

(Flavyl)(3-ethylthia)trimethylidenecyanine Perchlorate (X). A mixture of 0.102 g (0.25 mmole) of 4-(ω -anilino)vinylflavylum perchlorate and 0.087 g (0.25 mmole) of 1-ethyl-2-methylbenzothiazolium tosylate in a mixture of 2 ml of acetic anhydride and 0.1 ml of pyridine was heated at 120° for 1 h. The dye was removed by filtration and chromatographed with a column filled with aluminum oxide. The eluate was evapo-

rated, and the dye was reprecipitated from nitromethane by the addition of 20% perchloric acid and crystallized from the same solvent to give blue crystals with mp 162° (dec.). Found %: Cl 6.78. $C_{27}H_{22}ClNO_5S$. Calculated %: Cl 6.99.

(Senaflavylo)(3-ethylthia)trimethylidenecyanine Perchlorate (XII). A mixture of 0.191 g (0.5 mmole) of I, 0.225 g (0.5 mmole) of 1-ethyl-2-(ω -acetanilovinyl)benzothiazolium iodide, and 0.04 g (0.5 mmole) of anhydrous sodium acetate was heated in 2 ml of acetic anhydride-acetic acid (1:1) at 120° for 15 min. The dye was removed by filtration, washed with benzene and hot alcohol, and crystallized twice from alcohol-nitromethane (1:1) containing a drop of 20% perchloric acid to give 0.127 g (44%) of blue crystals with mp 272° (dec.). Found %: Se 13.82. $C_{27}H_{22}ClNO_4Se$. Calculated %: Se 13.84.

1-Ethyl-2-(2-phenyl-4'-benzoselenapyranilidene)methylbenzothiazolium Perchlorate (XIIIc). A mixture of 0.191 g (0.5 mmole) of I, 0.121 g (0.5 mmole) of 1-ethyl-2-sulfobenzothiazolium betaine, and 0.04 g (0.5 mmole) of anhydrous sodium acetate was heated in 2 ml of glacial acetic acid at 100-110° for 1 h. The dye was removed by filtration, washed with water and alcohol, and recrystallized from nitromethane to give 0.218 g (78%) of green crystals with mp 249° (dec.). Found %: Se 14.25. $C_{25}H_{20}ClNO_4SSe$. Calculated %: Se 14.50.

4-(p-Dimethylaminostyryl)senaflavylium Perchlorate (XIVc). This was obtained by heating 0.191 g (0.5 mmole) of I and 0.074 g (0.5 mmole) of p-dimethylaminobenzaldehyde in 2.5 ml of acetic anhydride at 100° for 15 min to give 0.22 g (85%) of green crystals with mp 215° (dec.) (from nitromethane). Found %: Se 15.59. $C_{25}H_{22}ClNO_4Se$. Calculated %: Se 15.35.

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