PYRYLOCYANINES

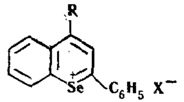
II.[*] SYMMETRICAL SELENOFLAVYLOCYANINES

A. I. Tolmachev and M. A. Kudinova

UDC 547.818.9

The reaction of selenoflavone with methylmagnesium iodide and with methyl o-nitrobenzenesulfonate was used to synthesize 4-methyl- and 4-methoxyselenoflavylium salts, from which a number of polymethine dyes of symmetrical structure were obtained. The selenoflavylocyanines have a considerably deeper color than other polymethine dyes with the same chromophore length.

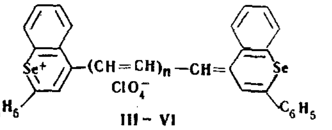
In this paper, we describe for the first time the synthesis and spectral properties of polymethine dyes that, except for selenium, do not contain other heteroatoms, viz., symmetrical selenoflavylocyanines. Information regarding their color is of interest for chromaticity theory. 4-Methyl- and 4-methoxyselenoflavylium salts (I and II) were used in the synthesis of the selenoflavylocyanines. Compound I was obtained by the reaction of selenoflavone with methylmagnesium iodide with subsequent treatment with perchloric acid, while II was obtained by the addition of methyl o-nitrobenzenesulfonate to the same base.



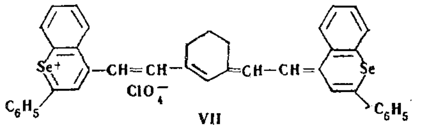
I, II

I $R = CH_3$, $X = ClO_4^-$;
II $R = OCH_3$, $X = o\text{-}NO_2C_6H_4SO_3^-$

Like their oxygen [2,3] and sulfur [1] analogs, the methyl group in the selenoflavylium salts is active with respect to electrophilic agents, while the methoxy group should be readily replaced by nucleophilic reagents. Using this, we obtained the symmetrical selenoflavylomonomethinylcyanine (III) by the condensation of I with II. Selenoflavone can also be used in place of II in the synthesis of III. Selenoflavylocarbocyanine (IV) was synthesized by heating I with ethyl orthoformate. Di- and tricarbocyanines (V and VI) are also formed by the reaction of I with the hydrochlorides of the dianils of malonic and glutaconic dialdehydes. Compound VI could not be isolated in the analytically pure state: it rapidly decomposes when dissolved in nitromethane, even at room temperature. However, by using the hydrochloride of the dianil of β,δ-trimethyleneglutaconic dialdehyde [4], we isolated selenoflavylotricarbocyanine (VII) in good yield; the six-membered hydrocarbon ring in the chromophore apparently stabilizes this sort of dye.



III - VI



VII

III $n = 0$, λ_{max} 744[†] nm (695)[‡]; IV $n = 1$, λ_{max} 835 nm (796); V $n = 2$, λ_{max} 935 nm (900);
VI $n = 3$, λ_{max} 1030 nm (1007); VII $n = 3$, λ_{max} 1035 nm

---

[*] See [1] for communication I.

[†] Here and elsewhere, the λ_{max} values are presented for solutions in nitromethane.

[‡] The λ_{max} values of the analogous thiaflavylocyanines are presented in parentheses; λ_{max} of thiaflavylotrimethinylcyanine is refined as compared with [1].

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 924-926, July, 1971. Original article submitted August 29, 1970.

The preparation of the dyes is accompanied by side processes, since I, like its sulfur analog [1], has high reactivity. Thus, monomethinylcyanine III forms in acetic anhydride when I is heated without any second component; a nonsalt dye with an absorption maximum at 480 nm is obtained instead of the expected hemicyanine when this salt is fused with dimethylformamidine. In order to suppress the side reactions in the synthesis of the selenoflavylocyanines, we used an excess of the second component. Just as in the case of thioflavylocyanines, alcohol solutions of the selenoflavylocyanines are unstable, while solutions of these dyes in nitromethane, chloroform, and glacial acetic acid are relatively stable.

Selenium-containing substituents ($SeCF_3$) in the heterocyclic residues in thiacarbocyanines have an auxochromic action very close to the analogous sulfur-containing substituents [5]. The absorption maxima of the selenocarbocyanines are shifted by 10 nm as compared with the absorption maxima of the analogous thiacarbocyanines [6]. In contrast to these dyes, the difference in the color between the symmetrical selenoflavylo- and thioflavylocyanines is considerably greater. The absorption maximum of IV is shifted by 39 nm to the long-wave region as compared with the sulfur analog and by 127 nm to the long-wave side as compared with its oxygen analog.* We also calculated the ratio of the zero and first moments for the long-wave absorption bands of the symmetrical flavylothioflavylo- and selenoflavylotrimethinylcyanines [7-9]:

$$M^{-1}=\frac{\int_{0}^{\infty} D_{\nu}\nu^{-1}d\nu}{\int_{0}^{\infty} D_{\nu}d\nu},$$

where M^{-1} is the ratio of the zero moment to the first moment, which determines the average position of the absorption band on the wavelength scale, and D is the optical density at the absorption band at frequency ν. These values prove to be 689.9, 763.8, and 801.8 nm, respectively, for trimethinylcyanines containing O, S, and Se. Consequently, the average position of the long-wave absorption band of selenoflavylotrimethinylcyanine is 34 nm more to the long-wavelength region than is the case for its sulfur analog and 112.7 nm more to the long-wavelength region than is the case for its oxygen analog. Thus, the cyanine dyes with selenoflavylium rings at the ends of the polymethine chain prove to be the most deeply colored of the yet known polymethine dyes with the same chromophore length. Two factors effect the color of the dyes under consideration: 1) the electronegativity of the heteroatom, which decreases in the order O > S > Se; 2) a decrease in the overlap of the orbitals of the heteroatom and the carbon atom in the same order. Quantum-mechanical calculations [10] indicate that for six-membered heterocyclic cations the first of these factors should induce a hypsochromic shift in the long-wave absorption band, while the second should produce a bathochromic shift in this band. In fact, the second effect predominates over the first [11, 12]. The deepening in the color in the order flavylo- < thioflavylo- < selenoflavylocyanines is apparently explained in the same way. The vinylene shifts in the selenoflavylocyanine series are close to the vinylene shifts in the thioflavylocyanine series, amount to 100 and 104 nm, respectively, on passing from n = 1 to n = 2.

EXPERIMENTAL

4-Methylselenoflavylium Perchlorate (I). A solution of a Grignard reagent obtained from 0.5 g (0.02 mole) of magnesium and 3 g (0.021 mole) of methyl iodide in 25 ml of absolute ether was added in the course of 20 min with mechanical stirring to a solution of 1.7 g (0.006 mole) of 1-selenoflavone [13] in 40 ml of absolute tetrahydrofuran. The mixture was heated at 40-50° for 2 h. It was then cooled, and a large portion of the solvent was removed by distillation. The residue was cooled with ice water, and 20% perchloric acid was added until the mixture gave an acid reaction to give 1.9 g (83%) of yellow crystals with mp 190° (decomp., from glacial acetic acid). Found %: Se 20.55. $C_{16}H_{13}ClO_4Se$. Calculated %: Se 20.59.

4-Methoxyselenoflavylium o-Nitrobenzenesulfonate (II). A mixture of 0.7 g (0.0024 mole) of selenoflavone and 0.54 g (0.0024 mole) of methyl o-nitrobenzenesulfonate [14] was heated at 100° for 2 h. The melt was triturated in a mortar with dry acetone, filtered, and washed with anhydrous ether to give 0.9 g (75%) of yellow crystals with mp 161° (glacial acetic acid). Found %: Se 16.16. $C_{22}H_{17}NO_6SeS$. Calculated %: Se 15.73.

---

*The λ_{max} value of the symmetrical flavylotrimethinylcyanine [2] in nitromethane is 708 nm.

Bis(4-selenoflavylo)monomethinylcyanine Perchlorate (III). A mixture of 0.191 g (0.0005 mole) of salt I and 0.250 g (0.0005 mole) of salt II was heated in 4 ml of acetic anhydride at 100° for 30 min. The dye was filtered, reprecipitated from solution in 10 ml of nitromethane by addition of 2.5 ml of 30% perchloric acid, and crystallized from acetic anhydride to give 0.322 g (99%) of shiny, green crystals with mp 132° (decomp.). Found %: Se 24.15. $C_{31}H_{21}ClO_4Se_2$. Calculated %: Se 24.28.

Bis(4-selenoflavylo)trimethinylcyanine Perchlorate (IV). A mixture of 0.383 g (0.001 mole) of salt I, 0.34 g (0.0025 mole) of ethyl orthoformate, and 0.3 g (0.0036 mole) of anhydrous sodium acetate in 5 ml of glacial acetic acid was refluxed for 30 min. The dye was filtered, washed with glacial acetic acid, and crystallized from nitromethane to give 0.282 g (41%) of shiny crystals with mp 265° (decomp.). Found %: Se 23.26. $C_{33}H_{23}ClO_4Se_2$. Calculated %: Se 23.35.

Bis(4-selenoflavyl)pentamethinylcyanine Perchlorate (V). A mixture of 0.152 g (0.0004 mole) of I, 0.05 g (0.0002 mole) of the dihydrochloride of the dianil of malonic dialdehyde and 0.03 g 0.00036 mole) of anhydrous sodium acetate in 4 ml of glacial acetic acid containing 3 ml of acetic anhydride was heated at 120° for 15 min. The dye was filtered, washed successively with glacial acetic acid and 250 ml of anhydrous benzene, and recrystallized twice from nitromethane to give 0.093 g (63%) of fine crystals with mp 253-254° (decomp.). Found %: Se 22.03. $C_{35}H_{25}ClO_4Se_2$. Calculated %: Se 22.34.

Bis(4-selenoflavylo)-11,13-trimethyleneheptamethinylcyanine Perchlorate (VII). This was obtained from the hydrochloride of the dianil of 2,4-trimethyleneglutaconic dialdehyde in the same way as V by heating for 1 h at 90-100°. The dye was filtered, washed successively with acetic anhydride, benzene, and ether, and crystallized from nitromethane to give 75% of dark-brown crystals. Found %: Se 20.28. $C_{40}H_{30}ClO_4Se_2$. Calculated %: Se 20.58.

LITERATURE CITED

1. A. I. Tolmachev and M. A. Kudinova, Khim. Geterotsikl. Soedin., 804 (1969).
2. R. Wizinger and H. Tobel, Helv. Chim. Acta, 40, 1305 (1957).
3. A. I. Kiprianov and A. I. Tolmachev, Zh. Obshch. Khim., 30, 638 (1960).
4. Yu. L. Slominskii, M. A. Kudinova, and A. I. Tolmachev, USSR Author's Certificate No. 299,503; Byull. Izobr., No. 12, 90 (1971).
5. L. M. Yagupol'skii and V. G. Voloshchuk, Ukr. Khim. Zh., 36, 66 (1970).
6. L. M. Clark, J. Chem. Soc., 216 (1933).
7. S. I. Kubarev, Dokl. Akad. Nauk SSSR, 130, 1067 (1960).
8. K. K. Rebane, Optika i Spektroskopiya, 9, 557 (1960).
9. B. I. Stepanov and V. P. Gribkovskii, Introduction to Luminescence Theory [in Russian], Minsk (1963), p. 156.
10. J. Fabian, A. Mehlhorn, and R. Zaradnik, Theoret. Chim. Acta, 12, 247 (1968).
11. J. Degani, R. Fochi, and C. Vinzenzi, Gazz. Chim. Ital., 94, 203 (1964).
12. J. Degani, R. Fochi, and G. Spunta, Boll. Sci. Fac. Chim. Ind., Bologna, 23, 165 (1965); Chem. Abstr., 63, 13,198 (1965).
13. A. Ruwet and M. Renson, Bull. Soc. Chim. Belge, 75, 200 (1966).
14. A. I. Kiprianov and A. I. Tolmachev, Zh. Obshch. Khim., 29, 2868 (1959).