PYRYLOCYANINES

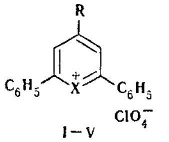
V.* UNSYMMETRICAL 2,6-PHENYL-SUBSTITUTED PYRYLO-, THIOPYRYLO-, AND SELENOPYRYLOCYANINES

A. I. Tolmachev, M. A. Kudinova,
and N. A. Derevyanko

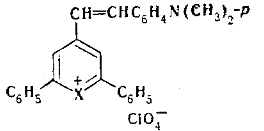
UDC 547.812.5.818.1.818.9

Unsymmetrical 2,6-diphenyl-substituted pyrylo-, thiopyrylo-, and selenopyrylotrimethinecyanines containing 1,3,3-trimethylindolinium or 3-methylbenzothiazolium nuclei have been synthesized. From the values of the deviations calculated from the long-wave absorption maxima and by the method of "bond moments," it follows that in the polymethine dyes the basicities of the heterocycles rise in the sequence: selenopyrylium < thiopyrylium < pyrylium. In view of the high electronic asymmetry of the dyes synthesized, in the long-wave bands of the absorption spectrum the strongest are the maxima corresponding to the first vibrational sublevel.

In a preceding communication symmetrical 2,6-diphenylthio- and 2,6-diphenylselenopyrylocyanines have been described [1]. For a more detailed investigation of the influence of the replacement of an oxygen atom by a sulfur or selenium atom in the pyrylocyanine series, in the present work we have obtained a number of unsymmetrical pyrylo-, thiopyrylo-, and selenopyrylocyanines. The initial compounds for the synthesis were 4-methyl-2,6-diphenyl-substituted pyrylium and thio- and selenopyrylium salts (I-III), and also 4-(ω-anilinovinyl)-2,6-diphenylthiopyrylium perchlorate (IV) and its selenium analog (V).



I – V



VI – VIII

I–III $R=CH_3$; IV,V $R=CH=CHNHC_6H_5$; I,VI $X=O$; II,IV,VII $X=S$; III,V,VIII $X=Se$

Compounds (IV) and (V) were synthesized by the reaction of the salts (II) and (III) with ethylisoformanilide. The p-dimethylaminostyryls (VI-VIII) were synthesized by the usual method – by the condensation of the salts (I-III) with p-dimethylaminobenzaldehyde [2]. 4-(p-Dimethylaminostyryl)-2,6-diphenylselenopyrylium perchlorate (VIII, λ_{max} 705 nm)† proved to be colored considerably more deeply than its sulfur analog (VII, λ_{max} 675 nm) and its oxygen analog (VI, λ_{max} 635 nm).

The unsymmetrical carbocyanines (IX), (X), and (XII) (Table 1) were obtained by the reaction of the pyrylium salt (I) with, respectively, 4-(ω-anilinovinyl) derivatives of 2,6-diphenylthio- and 2,6-diphenylselenopyrylium perchlorates (IV, V) and flavylium perchlorate. The trimethinecyanines (XI) and (XIII) were obtained by an analogous reaction starting from the selenopyrylium salt (III) and the hemicyanine (IV) or 4-(ω-anilinovinyl)selenoflavylium perchlorate. Compounds (XIV-XVI) were synthesized by condensing the

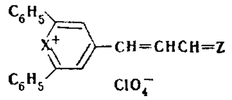
---

* For Communication IV, see [1].

† Here and below, the values of λ_{max} are given for solutions in nitromethane.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 53-57, January, 1974. Original article submitted October 25, 1972.

TABLE 1



Compound	X	Z	λ_{max}, nm	log ε	M^{-1}, nm	D, nm	D_M, nm
IX	S	2,6-Diphenylpyran-4-ylidene	715	5.19	684.1	0.5	–
X	Se	2,6-Diphenylpyran-4-ylidene	734	5.31	706.5	0.5	–
XI	Se	2,6-Diphenylthiopyran-4-ylidene	775	5.23	750.6	0	–
XII	O	2-Phenylbenzopyran-4-ylidene	683	5.16	–	9	–
XIII	Se	2-Phenylbenzoselenopyran-4-ylidene	800	5.0	–	15	–
XIV	O	1,3,3-Trimethylindolin-2-ylidene	585 625	4.91 4.96	582.3	14.5	8.6
XV	S	1,3,3-Trimethylindolin-2-ylidene	615 660	4.90 4.90	613.0	10	15.5
XVI	Se	1,3,3-Trimethylindolin-2-ylidene	630 675	4.89 4.81	618.3	−5	26.7
XVII	O	3-Ethylbenzothiazolin-2-ylidene	575 620	4.86 4.87	570.6	−3	27.9
XVIII	S	3-Methylbenzothiazolin-2-ylidene	605 648*	4.76 4.65	589.9	7.5	46.1
XIX	Se	3-Methylbenzothiazolin-2-ylidene	610 660*	4.81 4.63	592.1	15.5	60.3

*Shoulder.

salts (I-III) with 2-formylmethylene-1,3,3-trimethylindoline. The unsymmetrical thiacarbocyanines (XVII) were obtained by condensing pyrylium salt (I) with 2-(ω-acetanilidovinyl)-3-ethylbenzothiazolium iodide, and (XVIII) and (XIX) from the hemicyanines (IV and V) and 2,3-dimethylbenzothiazolium toluenesulfonate.

In order to determine the relative basicities of the residues of the oxygen-, sulfur, and selenium-containing six-membered heterocycles we have studied the deviations [3] of the carbocyanines obtained. In the case of the trimethinecyanines (IX-XI) (Table 1), constructed solely from pyrylium, thiopyrylium, and selenopyrylium residues, there is no deviation (D), which indicates the comparatively close basicities of the heterocyclic systems considered. The existence of deviations for the dyes (XII) and (XIII) is due to the fact that the fusion of a benzene ring to six-membered oxygen- or selenium-containing heterocycles is accompanied by a decrease in their basicity. For the unsymmetrical indo- and thiacarbocyanines (XIV-XIX), in addition to the calculation of the deviations with respect to the long-wave absorption maxima (D), as elsewhere in the literature [4, 5], we made use of the determination of the deviations from the mean positions of the absorption bands M^{-1} determined by the ratio of the zero and first moments of these bands (D_M) [6]. In the calculation of D and D_M, the values of λ_{max} and of M^{-1} for the symmetrical pyrylo-, thiopyrylo-, and selenopyrylocyanines were taken from [1], those for the symmetrical flavylo- and selenoflavylocyanines from [7], and those for the symmetrical thia-* and indocarbocyanines from [5]. The values of D for the dyes (XIV-XVI) and (XVII-XIX) calculated from the long-wave absorption maxima cannot be used to judge the comparative basicity of the O-, S-, and Se-containing heterocycles considered. For the carbocyanines (XVI, XVII), these magnitudes even have negative values. Conversely, the deviations D_M calculated by the method of band moments here give the correct characteristics. Depending on the nature of the heterocycle, both for the indocarbocyanines and for the thiacarbocyanines they increase on passing from oxygen to sulfur and selenium in the same way as in the analogous dyes containing flavylium, thioflavylium, and selenoflavylium residues [5]. Consequently, judging from the values of D_M, in the polymethine dyes the selenopyrylium nucleus is less basic than the thiopyrylium nucleus which, in its turn, behaves as less basic than the pyrylium nucleus.

The method of deviations in its general form proved inapplicable to the present case because of the marked difference in the shapes of the absorption curves of the dyes (XIV-XIX) and the symmetrical carbocyanines constructed from the same heterocyclic residues. As can be seen from Fig. 1, the absorption

---

*M^{-1} for 3,3-dimethylthiacarbocyanine is 538.7 nm.

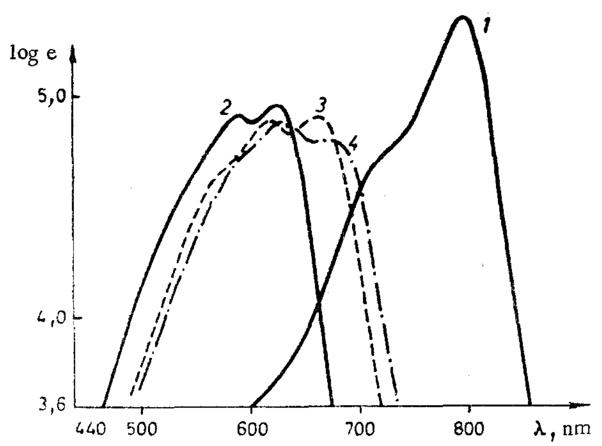


Fig. 1. Electronic absorption spectra of solutions in nitromethane: 1) bis-[2,6-diphenylselenopyrylo]-trimethinecyanine (XX); 2) [2,6-diphenylpyrylo]-[indo]-trimethinecyanine (XIV); 3) [2,6-diphenylthiopyrylo]-[indo]-trimethinecyanine (XV); 4) [2,6-diphenylselenopyrylo]-[indo]-trimethinecyanine (XVI).

curve of the symmetrical bis-[2,6-diphenylselenopyrylo-4]-trimethinecyanine (XX) has the shape typical for polymethine dyes [8-10] with a short-wave "secondary" maximum located at a distance of 1250 cm^{-1} from the main maximum. A similar shape of the curves is observed for the oxygen and sulfur analogs of the dye (XX) and of the unsymmetrical carbocyanines (IX-XIII) constructed from heterocycles of comparatively similar basicities.

Solutions in acetonitrile of the selenopyrylocyanine (XX), its oxygen and sulfur analogs, and the carbocyanines (IX-XI) possess intense luminescence (λ_{max} of the luminescence of dye (XX) is 840 nm). In all cases, the luminescence spectra showed a second maximum which is mirror-symmetrical with respect to the absorption spectra. This shows that the second maximum belongs to a vibrational sublevel of the same electronic transition.

The absorption curve of the unsymmetrical indocarbocyanines (XIV-XVI) each have two well-defined maxima (see Fig. 1 and Table 1). Attention is attracted by the facts that in the pyryloindotrimethinecyanine (XIV) the longer-wave maximum is still somewhat stronger than the short-wave maximum; in its sulfur analogs (XV) the two maxima have almost equal intensities; and in the least symmetrical indoselenopyrylotrimethinecyanine (XVI) the longer-wave maximum is now considerably weaker than the shorter-wave maximum. A complex shape of the curves is also observed for the unsymmetrical thiacarbocyanines (VII-XIX). The ratio of the intensities of the individual maxima in the solutions of these dyes does not depend on the concentration, which excludes an explanation of one of the bands by the state of aggregation of the dye. Under ordinary conditions, solutions of compounds (XIV-XIX) do not fluoresce. However, on the basis of the fact that, as for the symmetrical cyanines [11], the difference in the frequencies between the two maxima in the spectra of these dyes does not depend on the nature of the solvent (it is the same – approximately 1250 cm^{-1} – in nitromethane, chloroform, and nitrobenzene), it must be considered that in the dyes (XIV-XIX), as well, the two long-wave maxima belong to the same electronic transition. We have observed a similar shape of the absorption curves for unsymmetrical thia- and indocarbocyanines containing flavylium and thio- and selenoflavylium residues [5]. However, in the latter the intensity of the longer-wave maximum was still smaller, which must be connected with the greater electronic asymmetry of these dyes. Solutions of the carotenoids have absorption curves of similar shape [12]. Apparently, it is characteristic for solutions of all dyes in the molecules of which the carbon–carbon bonds of the chromophore differ strongly in their order. For example, the fact that in some tetra- and hexamethinemerocyanines a change in the polarity of the solvent causes, in addition to a shift in the absorption band itself, a change in the ratio of the intensities of the "main" and "auxiliary" maxima is undoubtedly connected with a change in the equivalence of the bonds of the chromophore [13].

EXPERIMENTAL

4-(ω-Anilinovinyl)-2,6-diphenylthiopyrylium Perchlorate (IV). A mixture of 0.725 g (2 mmoles) of (II) and 4 ml of ethylisoformanilide was heated at 70°C for 1 h. The precipitate was filtered off and was purified by chromatography from chloroform on alumina with subsequent precipitation from ethanolic solution with 20% perchloric acid and crystallization from glacial acetic acid. Yield 0.225 g (24%). Dark red needles with decomp. pt. 219-220°C, λ_{max} 512 nm. Found %: S 6.9. $C_{25}H_{20}ClNO_4S$. Calculated %: S 6.9.

4-(ω-Anilinovinyl)-2,6-diphenylselenopyrylium perchlorate (V) was obtained from (III) in a similar manner to (IV), but with heating at 50-55°C. Yield 62%. Dark red crystals with decomp. pt. 205-207°C (from glacial acetic acid), λ_{max} 532 nm. Found %: Se 15.4. $C_{25}H_{20}ClNO_4Se$. Calculated %: Se 15.4.

4-(p-Dimethylaminostyryl)-2,6-diphenylselenopyrylium Perchlorate (VIII). A mixture of 0.205 g (0.5 mmole) of (III) and 0.074 g (0.5 mmole) of p-dimethylaminobenzaldehyde in 2 ml of acetic anhydride was heated at 100-110°C for 30 min. Yield 0.230 g (85%). Green crystals with decomp. pt. 260°C. Found %: Se 14.4. $C_{27}H_{24}ClNO_4Se$. Calculated %: Se 14.6.

[2,6-Diphenylpyrylo-4]-[2,6-diphenylthiopyrylo-4]-trimethinecyanine Perchlorate (IX). A mixture of 0.230 g (0.6 mmole) of (I), 0.310 g (0.6 mmole) of (IV), and 0.054 g (0.6 mmole) of anhydrous sodium acetate in 4 ml of a 1:1 mixture of acetic anhydride and glacial acetic acid was heated at 130°C for 30 min. The dye was filtered off, reprecipitated from solution in nitromethane with 20% perchloric acid, and crystallized from acetic anhydride. Yield 3.60 g (87%). Lustrous green crystals with mp 288°C. Found %: S 5.1. $C_{37}H_{27}ClO_5S$. Calculated %: S 5.2.

[2,6-Diphenylpyrylo-4]-[2,6-diphenylselenopyrylo-4]-trimethinecyanine perchlorate (X) was obtained similarly to (IX), but heating was performed for 15 min. Yield 80%. Green needles with decomp.pt. 262°C (from a 1:1 mixture of acetic anhydride and acetic acid). Found %: Se 11.7. $C_{37}H_{27}ClO_5Se$. Calculated %: Se 11.9.

[2,6-Diphenylselenopyrylo-4]-[2,6-diphenylthiopyrylo-4]-trimethinecyanine perchlorate (XI) was obtained similarly to (IX) from the salts (III) and (IV) by heating for 1 h. Yield 72%. Golden needles with decomp.pt. 296°C (from acetic anhydride). Found %: Se 11.7. $C_{37}H_{27}ClO_4Se$. Calculated %: Se 11.6.

[2,6-Diphenylpyrylo-4]-[flavylo-4]-trimethinecyanine perchlorate (XII) was obtained similarly to (IX) from (I) and 4-(ω-anilinovinyl)flavylium perchlorate [14] with a yield of 70%. Dark green crystals with decomp. pt. 298°C (from a 1:1 mixture of acetic anhydride and acetic acid). Found %: Cl 6.1. $C_{35}H_{25}ClO_6$. Calculated %: Cl 6.1.

[2,6-Diphenylselenopyrylo-4]-[selenoflavylo-4]-trimethinecyanine perchlorate (XIII) was obtained similarly to (IX) from (III) and 4-(ω-anilinovinyl)selenoflavylium perchlorate [5] with a yield of 74%. Bronze crystals with decomp.pt. 271°C (from a 1:1 mixture of acetic anhydride and acetic acid). Found %: Se 22.2. $C_{35}H_{25}ClO_4Se_2$. Calculated %: Se 22.5.

[2,6-Diphenylpyrylo-4]-[1,3,3-trimethylindo-2]-trimethinecyanine Perchlorate (XIV). A mixture of 0.173 g (0.5 mmole) of (I), 0.1 g (0.5 mmole) of 2-formylmethylene-1,3,3-trimethylindoline, and 0.04 g (0.5 mmole) of anhydrous sodium acetate was heated in 2 ml of a 1:1 mixture of acetic anhydride and acetic acid at 130°C for 15 min. The dye was filtered off, reprecipitated from acetic acid solution with 42% perchloric acid, and crystallized from the same solvent. Yield 0.160 g (60%). Green crystals with decomp. pt. 231°C. Found %: Cl 6.5. $C_{31}H_{28}ClNO_5$. Calculated %: Cl 6.7.

[2,6-Diphenylthiopyrylo-4]-[1,3,3-trimethylindo-2]-trimethinecyanine perchlorate (XV) was obtained similarly to (XIV) from (II). Yield 90%. Lustrous green needles with decomp.pt. 231°C (from glacial acetic acid). Found %: S 5.9. $C_{31}H_{28}ClNO_4S$. Calculated %: S 5.9.

[2,6-Diphenylselenopyrylo-4]-[1,3,3-trimethylindo-2]-trimethinecyanine perchlorate (XVI) was obtained similarly to (XIV) from (III). Yield 80%. Lustrous green needles with decomp.pt. 236°C (from a mixture of nitromethane and ethanol). Found %: Se 13.2. $C_{31}H_{28}ClNO_4Se$. Calculated %: Se 13.3.

[2,6-Diphenylpyrylo-4]-[3-ethylthia-2]-trimethinecyanine Perchlorate (XVII). A mixture of 0.190 g (0.54 mmole) of (I), 0.240 g (0.54 mmole) of 2-(ω-acetanilinovinyl)-3-ethylbenzothiazolium iodide, and 0.2 ml (0.14 g, 1 mmole) of triethylamine in 6 ml of absolute ethanol was boiled for 5 min. The dye was filtered off and was crystallized from glacial acetic acid. Yield 0.092 g (36%). Dark blue needles with decomp. pt. 232°C. Found %: Cl 6.45. $C_{29}H_{24}ClNO_5S$. Calculated %: Cl 6.65.

[2,6-Diphenylthiopyrylo-4]-[3-methylthia-2]-trimethinecyanine Perchlorate (XVIII). A mixture of 0.232 g (0.5 mmole) of the hemicyanine (IV), 0.184 g (0.54 mmole) of 2,3-dimethylbenzothiazolium toluenesulfonate, and 0.04 g (0.5 mmole) of anhydrous sodium acetate in 7 ml of a 1:1 mixture of acetic anhydride and acetic acid was heated at 100°C for 5 min. The dye was filtered off and was chromatographed from a 1:1 mixture of chloroform and nitromethane on alumina, was reprecipitated from solution in a 1:1 mixture of ethanol and nitromethane with 20% perchloric acid, and was crystallized from a 1:3 mixture of acetic anhydride and acetic acid. The yield was 0.180 g (60%). Dark blue crystals with decomp.pt. 283°C. Found %: S 11.8. $C_{28}H_{22}ClNO_4S_2$. Calculated %: S 11.9.

[2,6-Diphenylselenopyrylo-4]-[3-methylthia-2]-trimethinecyanine perchlorate (XIX) was obtained similarly to (XVIII) from the hemicyanine (V) and 2,3-dimethylbenzothiazolium toluenesulfonate, except that the mixture was heated for 15 min. Yield 86%. Green needles with decomp.pt. 249°C (from a 1:1 mixture of nitromethane and ethanol). Found %: Se 13.4. $C_{28}H_{22}ClO_4SSe$. Calculated %: Se 13.6.

LITERATURE CITED

1. A. I. Tolmachev and M. A. Kudinova, Khim. Geterotsikl. Soedin., 49 (1974).
2. R. Wizinger and P. Ulrich, Helv. Chim. Acta, 39, 207 (1956).

3. A. I. Kiprianov, Introduction to the Electronic Theory of Organic Compounds [in Russian], Naukova Dumka, Kiev (1965), p. 156.
4. E. D. Sych, Zh. N. Belaya, and G. G. Dyadyusha, Ukr. Khim. Zh., 30, 1065 (1964).
5. A. I. Tolmachev and M. A. Kudinova, Khim. Geterotsikl. Soedin., 1177 (1971).
6. B. I. Stepanov and V. L. Gribkovskii, Introduction to the Theory of Luminescence [in Russian], Minsk (1963), p. 156.
7. A. I. Tolmachev and M. A. Kudinova, Khim. Geterotsikl. Soedin., 924 (1971).
8. S. I. Vavilov, Sobr. Soch., Izd. Kad. Nauk SSSR, 1, 105 (1952).
9. A. I. Terenin, The Photonics of Dye Molecules [in Russian], Nauka, Leningrad (1967), p. 177.
10. J. Pouradier, J. Chem. Phys., 61, 1107 (1964).
11. W. West and A. Geddes, J. Phys. Chem., 68, 837 (1964).
12. O. Isler, R. Ruegg, and P. Schudel, Chimia, 15, 208 (1961).
13. F. A. Gershtein, Z. P. Sytnik, I. I. Levkoev, É. B. Lifshits, L. O. Leont'eva, and Yu. S. Rozum, in: Collection of Scientific Papers on the Synthesis, Treatment, and Investigation of Special Organic Compounds for the Photographic Chemicals Industry [in Russian], Moscow, No. 7 (1972), p. 4.
14. R. Wizinger and W. Heldemann, Chem. Ber., 93, 7 (1960).