PYRYLOCYANINES

IV.* SYMMETRICAL 2,6-DIPHENYLTHIO- AND 2,6-DIPHENYLSELENOPYRYLOCYANINES

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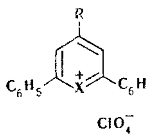
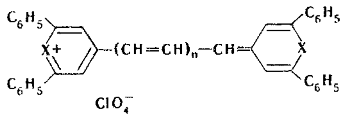
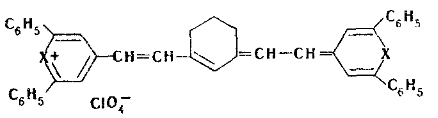
From 4-methyl-2,6-diphenylthiopyrylium and 4-methyl-2,6-diphenylselenopyrylium salts thio- and selenopyrylocyanines with symmetrical structures have been synthesized. In the series of dyes synthesized, greater values of the vinylidene shifts of the absorption maxima are observed than in the series of their thio- and selenoflavylium analogs. The mono-, tri-, and pentamethinecyanines obtained are more highly colored than the analogous thio- and selenoflavylocyanines and, conversely, the 2,6-diphenylselenopyryloheptamethinecyanines are colored less deeply than the selenoflavylotricarbocyanines. The structure of the product of the oxidation of 4-methyl-2,6-diphenylpyrylium perchlorate has been established.

We have recently described polymethine dyes containing no heteroatoms other than selenium – selenoflavylocyanines [1, 2] – which proved to be the most deeply colored among the known polymethine dyes with the same length of chromophore. It appeared of interest to investigate the influence on the color of the replacement of the oxygen atom of a heterocycle by a sulfur or selenium atom in the pyrylocyanines, also. For this purpose, in the present work we have obtained 2,6-diphenylthio- and 2,6-diphenylselenopyrylocyanines. It is known that solutions of some pyrylocyanines can be used as Q switches for lasers (QSLs). [3]. Since thiopyrylium and selenopyrylium salts are more stable to hydrolysis than pyrylium salts [4], and, judging from the basicity of the pyrones [5], than their benzo homologs, solutions of such dyes could also be of interest for use in QSLs. Thiopyrylomono- and thiopyrylotrimethinecyanines have been synthesized previously by the condensation of 2,6-diphenylthiopyrylium perchlorate with dibasic acids [6]. It has not yet been possible to obtain pentamethinecyanines in the pure state in this way [6]. Selenopyrylocyanines were completely unknown.

We have synthesized thiopyrylotri-, -penta-, and -heptamethinecyanines (VII, IX, and XI) by the reaction of 4-methyl-2,6-diphenylthiopyrylium perchlorate (I) with orthoformic ester (as in [7]) or with the hydrochlorides of the dianils of malondialdehyde and glutacondialdehyde. The bis(2,6-diphenylselenopyrylo-4)-monomethinecyanine (V) was obtained by condensing 4-methyl-2,6-diphenylselenopyrylium perchlorate (II) [8] with 2,6-diphenylselenopyrylium perchlorate (III) [8]. The selenopyrylotri-, -penta-, and -heptamethinecyanines (VIII, X, and XII) were synthesized by using the selenopyrylium salt (II) in the same way as their sulfur analogs. In addition to tricarbocyanines with open polymethine chains (XI, XII), the use of the hydrochloride of the dianil of β,δ-trimethyleneglutacondialdehyde [9] also gave the thio- and selenopyrylium tricarbocyanines (XIII and XIV) containing a six-membered carbon ring in the chromophore.


I-III


IV-XI


XIII, XIV

I X=S; II, III X=Se; I, II R=CH_3; III R=H

The thio- and selenopyrylium salts (I and II) are distinguished by a high reactivity, thanks to which the synthesis

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*For Communication III, see [1].

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TABLE 1. Absorption Maxima of the Pyrylocyanines in Nitromethane

Compound	n	X	λ_{max}, nm*
IV	0	S	627[6] (695)*
V	0	Se	672 (744)
VI	1	O	676† (708)[2]
VII	1	S	755† (796)
VIII	1	Se	795 (835)
IX	2	S	879 (900)
X	2	Se	910 (935)
XI	3	S	1000 (1007)
XII	3	Se	1035 (1030)
XIII	—	S	1017 —
XIV	—	Se	1050 (1035)

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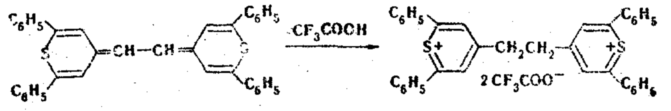
* The values of λ_{max} for the analogous thioflavylocyanines [10] and selenoflavylocyanines are given in parentheses.

† Figure refined as compared with that given by Wizinger and Heldemann [11].

of polymethine dyes from them is accompanied by side reactions. One of the side reactions is the oxidation of the 4-methylene-2,6-diphenyl-4H-pyrans formed from these salts under the action of bases. Thus, when a suspension of the salt (I) in acetone was treated with alkali, a high yield of 1,2-bis(2,6-diphenylthiopyran-4-ylidene)ethane (XV) was obtained. Here the reaction probably takes place in a similar manner to the oxidation of 1,1,3-trimethyl-2H-indole [12], except that it does not require a special oxidizing agent. The structure of (XV) was confirmed by PMR spectroscopy. In solution in phosphoric tris(dimethylamide), the spectrum of (XV) contains three singlets, with chemical shifts of 8.53 ppm (2H), 7.12 ppm (2H), and 6.72 ppm (2H) and a multiplet between 7.75 and 7.20 ppm (20 H). The signal at 6.72 ppm we assign to the protons of the ethanediylidene group, the multiplet at 7.75-7.20 ppm to the protons of the phenyl groups, and the singlets at 8.53 and 7.12 ppm to the protons present in the 3,5- positions of the thiopyran rings. These protons are nonequivalent because of the absence of free rotation of the heterocyclic residues in the molecule. In trifluoroacetic acid solution, the base (XV) adds two protons, forming the cation (XVI), the PMR spectrum of which contains singlets at 8.80 ppm (4H, Het–H) and 3.90 ppm (4H, $2CH_2$) and a multiplet at 8.05-7.53 ppm (20H, $4C_6H_5$).



XV XVI

In agreement with this is the fact that in the spectrum of the salt (I) the signal of the protons attached to the β-carbon atoms of the heterocycle is located at 8.78 ppm, that of the aromatic protons at 8.23-7.72 ppm, and that of the methyl group at 3.20 ppm. It must be mentioned that a compound analogous to (XV) is also formed by heating 4-methylthioflavylium perchlorate in dimethylformamide or pyridine with yields of 90 and 70%, respectively. Consequently, in spite of the opinion of Van Allan and Reynolds [13, 14] it must be assumed for this case, also, that oxidation is brought about by atmospheric oxygen. A compound analogous to (XV) with its absorption maximum at 526 nm is also formed from the selenopyrylium salt (II).

Ethanolic solutions of the thio- and selenopyrylocyanines, like the thio- and selenoflavylocyanines, are unstable; solutions of these dyes in nitromethane, chloroform, and glacial acetic acid are relatively stable.

The absorption maxima of the selenopyrylocyanines (V, VIII, X, and XII), like those of the selenoflavylocyanines, are located in the longer-wave region than the absorption maxima of their sulfur analogs (IV, VII, IX, and XI), which, in their turn, are more deeply colored than the dyes constructed from oxygen heterocycles (Table 1). In the carbocyanines (VI–VIII), the shifts of the long-wave absorption maximum on passing from the pyrylo- to the thiopyrylo- and selenopyrylocyanines are 79 and 119 nm, respectively. For the trimethinecyanines (VI–VIII) we also calculated the values of M^{-1} – the ratio of the zero moments to the first moments, which determine the average position of the absorption bands in the wavelengths scale [2]. For the trimethinecyanines containing O, S, and Se, M^{-1} proved to be, respectively, 657.8, 733.1, and 766.1 nm, i.e., the shifts of the mean position of the long-wave absorption band on passing from the dye (VI) to the dyes (VII) and (VIII) are, respectively, 75.3 and 108 nm. As can be seen from the figures given, the vinylene shift of the long-wave absorption band in the 2,6-diphenylthio- and 2,6-diphenylselenopyrylocyanines is approximately 120-125 nm. In the flavylium analogs of these dyes, however, it is only 100 nm. While the absorption maxima of the pyrylomonomethinecyanines (IV, V) are located 70 nm towards the shorter-wave region as compared with the absorption maxima of their flavylium analogs, in the carbocyanines, in view of the dissimilar vinylene shifts, this difference (VII and VIII) falls to 40 nm and in the dicarbocyanines (IX and X) to 20-25 nm. Conversely, the 2,6-diphenylselenopyrylocyanines (XII and XIII) are colored still more deeply than their selenoflavylium analogs and, thus, are the most deeply colored of the known polymethine dyes with the same length of chromophore.

EXPERIMENTAL

The PMR spectra were taken on a ZKR-60 spectrophotometer with a working frequency of 60 MHz at a temperature of 29°C and a concentration of 0.12 M. The chemical shifts are given relative to TMS (internal standard).

Bis(2,6-diphenylselenopyrylo-4)monomethinecyanine Perchlorate (V). A mixture of 0.204 g (0.5 mmole) of 4-methyl-2,6-diphenylselenopyrylium perchlorate (II), 0.196 g (0.5 mmole) of 2,6-diphenylselenopyrylium perchlorate (III), and 0.04 g (0.5 mmole) of anhydrous sodium acetate in 4 ml of glacial acetic acid was heated at 100°C for 30 min. The dye was filtered off, reprecipitated from solution in nitromethane with 42% perchloric acid, and crystallized from acetic anhydride. Yield 0.22 g (62%). Green crystals with mp 268°C. Found %: Se 22.4. $C_{35}H_{25}ClO_4Se_2$. Calculated %: Se 22.5.

Bis(2,6-diphenylselenopyrylo-4)trimethinecyanine Perchlorate (VIII). A mixture of 0.408 g (1 mmole) of (II), 0.296 g (2 mmoles) of orthoformic ester, and 0.082 g (1 mmole) of anhydrous sodium acetate in 6 ml of glacial acetic acid was heated at 120°C for 10 min. Yield 0.36 g (98%). Bronze crystals with decomp. pt. 291°C (from acetic anhydride). Found %: Se 21.4. $C_{37}H_{27}ClO_4Se_2$. Calculated %: Se 21.7.

Bis(2,6-diphenylthiopyrylo-4)pentamethinecyanine Perchlorate (IX). A solution of 0.129 g (0.5 mmole) of the hydrochloride of the dianil of malondialdehyde in 25 ml of acetic anhydride was added to a solution of 0.362 g (1 mmole) of (I) and 0.082 g (1 mmole) of anhydrous sodium acetate in 5 ml of acetic acid, and the mixture was heated at 110°C for 30 min. The dye was separated off and was washed free from contaminating monomethinecyanine with hot acetic acid. After crystallization from nitromethane, the product formed lustrous green crystals. Yield 24%. Found %: Cl 5.1. $C_{39}H_{29}ClO_4S_2$. Calculated %: Cl 5.3.

Bis(2,6-diphenylselenopyrylo-4)pentamethinecyanine perchlorate (X) was obtained similarly to (IX) from 0.204 g (0.5 mmole) of (II) in 4 ml of a mixture of acetic anhydride and glacial acetic acid (1:1). Yield 60%. Found %: Se 21.3. $C_{39}H_{29}ClO_4Se_2$. Calculated %: Se 20.9.

Bis(2,6-diphenylthiopyrylo-4)pentamethinecyanine Perchlorate (XI). A solution of 0.56 g (2 mmoles) of the hydrochloride of the dianil of glutacondialdehyde in 15 ml of acetic anhydride was added to a solution of 0.362 g (1 mmole) of (I) in 15 ml of the same solvent at 20°C, and the mixture was left in the dark. After 12 h, the dye was filtered off and was washed with acetic anhydride, with dry benzene, and with ether. Yield 0.04 g (12%). Brown crystals. Found %: Cl 5.2. $C_{41}H_{31}ClO_4S_2$. Calculated %: Cl 5.2.

Bis(2,6-diphenylselenopyrylo-4)heptamethinecyanine perchlorate (XII) was obtained in a similar manner to (XI) from 0.204 g (0.5 mmole) of (II). Yield 50%. Found %: Se 20.2. $C_{41}H_{31}ClO_4Se_2$. Calculated %: Se 20.2.

Bis(2,6-diphenylthiopyrylo-4)-9,11-trimethyleneheptamethinecyanine Perchlorate (XIII). A solution of 0.064 g (0.2 mmole) of the hydrochloride of the dianil of 2,4-trimethyleneglutacondialdehyde in 3 ml of acetic anhydride was added to a suspension of 0.145 g (0.4 mmole) of (I) and 0.032 g (0.4 mmole) of anhydrous sodium acetate in 3 ml of glacial acetic acid, and the mixture was heated at 90-100°C for 1 h. The dye was filtered off and was washed with acetic anhydride with benzene, and with ether, and was crystallized from nitromethane. Yield 37%. Found %: S 8.9. $C_{44}H_{35}ClO_4S_2$. Calculated %: S 8.8.

Bis(2,6-diphenylselenopyrylo-4)-9,11-trimethyleneheptamethinecyanine perchlorate (XIV) was obtained similarly to (XIII) from (II) with 30 min heating of the solution. Yield 50%. Found %: Se 18.9. $C_{44}H_{35}ClO_4Se_2$. Calculated %: Se 19.2.

1,2-Bis(2,6-diphenylthiopyran-4-ylidene)ethane (XV). A suspension of 0.724 g (2 mmoles) of (I) and 0.4 g (10 mmoles) of caustic soda in a mixture of 15 ml of acetone and 2 ml of water was shaken until the solid matter had dissolved completely. Then the organic layer was separated off, filtered, and diluted with ice water. The product that then deposited was filtered off and recrystallized from dimethylformamide. Yield 0.877 g (84%). Lustrous dark red needles with decomp. pt. 258°C. λ_{max} 512 nm. Found %: C 82.8; H 5.0; S 12.1. $C_{36}H_{26}S_2$. Calculated %: C 82.8; H 5.0; S 12.3.

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