# PYRYLOCYANINES.

## 14.* UNSYMMETRICAL PYRYLOCYANINES BASED ON 2,3-POLYMETHYLENE-4,6-DIPHENYLPYRYLIUM SALTS

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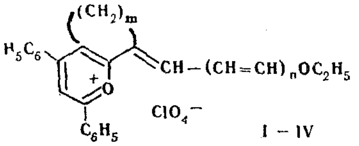
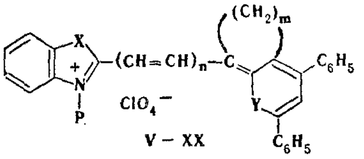
Unsymmetrical 4,6-diphenylpyrylo-2-carbo- and dicarbocyanines, as well as the analogous pyridocyanines, containing 3-ethylbenzothiazolium and 1,3,3-trimethyl-3H-indolium residues and an ethylene or trimethylene bridging grouping between the α position of the polymethine chain and the β position of the pyrylium or pyridinium residue were synthesized. The introduction of bridging groups is generally accompanied by a bathochromic effect and intensification (in the pyrylocyanine series) or weakening (in the pyridocyanine series) of the fine structure of the absorption bands. On the basis of the deviations calculated from the centers of the absorption bands and the dependences of the vinylene shifts and the absorption band widths on the structure of the dyes it was concluded that the trimethylene bridging groups in the examined cases increase the electron-donor character of the heterocyclic residues in the dyes more markedly than the ethylene bridging groups.

Symmetrical pyrylo-2-, thiopyrylo-2-, and pyrido-2-cyanines in which the α positions of the polymethine chromophore are bonded to the β-carbon atoms of the heterocyclic residues by ethylene or trimethylene groupings were described in [1]. For a more detailed study of the effect of bridging groupings on the color we accomplished the synthesis of a number of pyrylo- and pyridocyanines with unsymmetrical structures containing the same groupings by means of salts with structures I-IV. Pyrylocarbo- (V, IX) and -dicarbocyanines (VI, X) (Table 1), which contain ethylene groupings, were obtained by condensation of ethoxyvinyl- and ethoxybutadienyl-substituted pyrylium salts (I, II) with 1,2,3,3-tetramethyl-3H-indolium or 2-methyl-3-ethylbenzothiazolium salts in the same way as their analogs (VII, VIII, XI, and XII) with trimethylene groupings, which were synthesized by the method in [2]. Unsymmetrical pyridocyanines XIII-XX were obtained by treatment of the corresponding pyrylocyanines with methylamine.

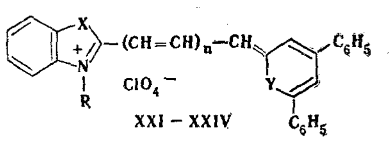


I – IV

I n=0, m=2; II n=1, m=2; III n=0, m=3; IV n=1, m=3



V – XX



XXI – XXIV

X = $C(CH_3)_2$, S; Y = O, $NCH_3$; R = $CH_3$, $C_2H_5$; n = 1, 2

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*See [1] for Communication 13.

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TABLE 1. Characteristics of the Long-Wave Absorption Bands of Dyes V-XXVIII IN $CH_2Cl_2$

| Compound | X | Y | R | m | n | $\lambda_{max}$, nm (log ε) | $M^{-1}$, nm | $D_M$, nm | f | σ, cm$^{-1}$ | $\gamma_1$ | $\gamma_2$ | F |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| V | $C(CH_3)_2$ | O | $CH_3$ | 2 | 1 | 662; 718 (4,84; 4,78) | 656,5 | 6,8 | 0,88 | 1360 | 1,09 | 2,2 | 0,052 |
| VI | $C(CH_3)_2$ | O | $CH_3$ | 2 | 2 | 758; 822 (5,01; 5,05) | 761,3 | 0,8 | 1,17 | 1190 | 1,22 | 2,7 | 0,059 |
| VII | $C(CH_3)_2$ | O | $CH_3$ | 3 | 1 | 660; 706 (4,76; 4,68) | 651,6 | 2,4 | 0,78 | 1380 | 1,01 | 2,0 | 0,039 |
| VIII | $C(CH_3)_2$ | O | $CH_3$ | 3 | 2 | 756; 807 (4,93; 4,97) | 753,9 | −2,1 | 1,04 | 1170 | 1,18 | 2,6 | 0,050 |
| IX | S | O | $C_2H_5$ | 2 | 1 | 667; 724 (4,84; 4,72) | 650,9 | 22,0 | 0,86 | 1490 | 1,22 | 2,8 | 0,061 |
| X | S | O | $C_2H_5$ | 2 | 2 | 755; 824 (5,00; 4,97) | 741,7 | 28,1 | 1,23 | 1430 | 1,34 | 3,1 | 0,072 |
| XI | S | O | $C_2H_5$ | 3 | 1 | 666; 714 (4,70; 4,57) | 650,5 | 13,0 | 0,69 | 1470 | 1,03 | 2,1 | 0,041 |
| XII | S | O | $C_2H_5$ | 3 | 2 | 750; 818 (4,90; 4,86) | 740,9 | 18,7 | 1,03 | 1350 | 1,10 | 2,1 | 0,050 |
| XIII | $C(CH_3)_2$ | $NCH_3$ | $CH_3$ | 2 | 1 | 580 (4,88) | 564,3 | 44,6 | 0,81 | 1160 | 1,04 | 2,2 | 0,034 |
| XIV | $C(CH_3)_2$ | $NCH_3$ | $CH_3$ | 2 | 2 | 654 (4,97) | 627,9 | 76,5 | 1,10 | 1320 | 1,19 | 2,7 | 0,045 |
| XV | $C(CH_3)_2$ | $NCH_3$ | $CH_3$ | 3 | 1 | 560 (4,66) | 545,5 | 53,1 | 0,65 | 1430 | 1,00 | 2,2 | 0,034 |
| XVI | $C(CH_3)_2$ | $NCH_3$ | $CH_3$ | 3 | 2 | 612 (4,69) | 592,6 | 105,5 | 0,82 | 1730 | 1,12 | 2,5 | 0,047 |
| XVII | S | $NCH_3$ | $C_2H_5$ | 2 | 1 | 598 (4,89) | 586,1 | 32,3 | 0,79 | 1220 | 0,83 | 2,7 | 0,041 |
| XVIII | S | $NCH_3$ | $C_2H_5$ | 2 | 2 | 685 (5,04) | 657,2 | 54,9 | 0,87 | 1220 | 1,21 | 2,7 | 0,047 |
| XIX | S | $NCH_3$ | $C_2H_5$ | 3 | 1 | 588 (4,70) | 572,1 | 36,0 | 0,64 | 1410 | 1,03 | 2,6 | 0,039 |
| XX | S | $NCH_3$ | $C_2H_5$ | 3 | 2 | 650 (4,72) | 625,8 | 80,0 | 0,81 | 1670 | 1,24 | 3,1 | 0,055 |
| XXI | $C(CH_3)_2$ | O | $CH_3$ | — | 1 | 654; 682 (4,71; 4,30) | 641,1 | −8,3 | 0,76 | 1450 | 0,89 | 1,5 | 0,031 |
| XXII | $C(CH_3)_2$ | O | $CH_3$ | — | 2 | 750; 796 (4,97; 4,87) | 740,2 | −5,8 | 1,18 | 1280 | 0,86 | 1,3 | 0,030 |
| XXIII | S | O | $C_2H_5$ | — | 1 | 658; 708 (4,73; 4,53) | 636,9 | 5,5 | 0,84 | 1530 | 0,84 | 1,3 | 0,029 |
| XXIV | S | O | $C_2H_5$ | — | 2 | 748; 815 (4,91; 4,74) | 721,0 | 21,1 | 1,14 | 1540 | 1,00 | 1,8 | 0,042 |
| XXV | $C(CH_3)_2$ | $NCH_3$ | $CH_3$ | — | 1 | 550 (4,84) | 538,0 | 27,3 | 0,72 | 1160 | 1,17 | 2,8 | 0,046 |
| XXVI | $C(CH_3)_2$ | $NCH_3$ | $CH_3$ | — | 2 | 630 (4,91) | 607,3 | 58,3 | 0,93 | 1290 | 1,35 | 3,4 | 0,058 |
| XXVII | S | $NCH_3$ | $C_2H_5$ | — | 1 | 575 (4,98) | 558,5 | 16,4 | 0,88 | 1040 | 1,16 | 2,7 | 0,055 |
| XXVIII | S | $NCH_3$ | $C_2H_5$ | — | 2 | 660 (5,06) | 638,3 | 35,0 | 1,08 | 1140 | 1,36 | 3,4 | 0,058 |

TABLE 2. Characteristics of the Synthesized Compounds

| Compound | Dec. temp., °C | Found, % | | Empirical formula* | Calc., % | | Yield, % |
|---|---|---|---|---|---|---|---|
| | | Cl | N(S) | | Cl | N(S) | |
| I | 174—175 | 8,0 | — | $C_{23}H_{21}ClO_6$ | 8,0 | — | 44 |
| V | 245—247 | 6,5 | — | $C_{33}H_{30}ClNO_5$ | 6,2 | — | 67 |
| VI | 205—206 | 6,3 | — | $C_{35}H_{32}ClNO_5$ | 6,1 | | 90 |
| IX | 265 | 6,3 | (5,8) | $C_{31}H_{26}ClNO_5S$ | 6,3 | (5,7) | 70 |
| X | 231—233 | 6,3 | (5,4) | $C_{33}H_{28}ClNO_5S$ | 6,1 | (5,5) | 63 |
| XIII | 174 | 6,6 | 5,0 | $C_{34}H_{33}ClN_2O_4$ | 6,2 | 4,9 | 88 |
| XIV | 224—225 | 5,9 | 4,9 | $C_{36}H_{35}ClN_2O_4$ | 6,0 | 4,7 | 87 |
| XV | 204 | 6,1 | 5,0 | $C_{35}H_{35}ClN_2O_4$ | 6,1 | 4,8 | 96 |
| XVI | 240—242 | 5,8 | 4,6 | $C_{37}H_{37}ClN_2O_4$ | 5,8 | 4,6 | 83 |
| XVII | 238—239 | 6,3 | 4,9 | $C_{32}H_{29}ClN_2O_4S$ | 6,2 | 4,9 | 88 |
| XVIII | 162 | 6,1 | 4,8 | $C_{34}H_{31}ClN_2O_4S$ | 5,9 | 4,7 | 78 |
| XIX | 202—204 | 5,9 | (5,5) | $C_{33}H_{31}ClN_2O_4S$ | 6,1 | (5,5) | 94 |
| XX | 215 | — | 4,6 | $C_{35}H_{33}ClN_2O_4S$ | — | 4,6 | 93 |

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*The composition of dye V was also confirmed by analysis for C andH (andfor S in the case of dye XX).

The spectral characteristics* of dyes V-XX and their analogs XXI-XXIV [3] which are not substituted in the chromophore chain, are compared in Table 1. In comparing the average values of the absorption bands ($M^{-1}$) it is apparent that, except for pyridodicarbocyanines XVI and XX, the dyes obtained, like the symmetrical dyes described in [1], are more deeply colored than their unsubstituted analogs; the effect from the ethylene groupings is somewhat greater than from the trimethylene groupings. In the pyrylocyanine series the bathochromic effect of the bridging groupings increases somewhat on passing from the carbocyanines to the dicarbocyanines, whereas in the case of pyridocyanines, on the other hand, it decreases.

The analysis of the data presented in Table 1 is complicated by the fact that the groupings under consideration have not only an electronic effect but also a steric effect on the absorption of light by the dyes; the steric hindrance created by these groupings differs in carbocyanines with symmetrical and unsymmetrical structures. Nevertheless, it seemed of interest to attempt, on the basis of the spectral data, to draw a conclusion regarding the effect of annelated five- and six-membered rings on the "basicities" of the heterocyclic residues in the dyes. Since the polymethylene groupings in dyes V-XX can be regarded as electron-donor substituents in even-numbered positions of the chromophore, they should increase the "basicities" of the heteroresidues adjacent to them. However, it is difficult to state beforehand which of the groups (the ethylene or trimethylene group) will have the greater effect. It is not possible to solve this problem on the basis of the deviations ($D_M$) of the synthesized pyrylocyanines, since no clear regularity is observed in the changes in this characteristic in this case. As we noted in [3], this is due primarily to the fact that the method of deviations is strictly applicable only in those cases in which the absorption bands of symmetrical dyes constructed from the same heterocycles as the unsymmetrical dye under consideration are located in the same spectral region. However, in the given case they are separated by a distance of more than 250 nm from one another. In contrast to pyrylocyanines, a distinct regularity is observed in the deviations of unsymmetrical pyridocyanines, for which the corresponding symmetrical dyes absorb in closer regions. In the series of these dyes, both substituted (XIII-XX) and unsubstituted (XXV-XXVIII), replacement of the thiazolium residue by an indolium residue, owing to an increase in the electronic asymmetry of the dye, and lengthening of the polymethine chain lead to an increase in the deviations. It is important that the deviations are greater for the dyes with cyclic groupings than for their unsubstituted analogs; the introduction of trimethylene groupings gives rise to a greater increase in the deviation than the introduction of ethylene groupings. These data confirm that annelation of both the five-membered and six-membered rings leads to an increase in the "basicity" of the heteroring in the dyes; a six-membered ring has a greater effect.

The observed tendency for a change in the vinylene shifts and the widths of the absorption bands is also in agreement with the increase in the electron-conor character under the influence of bridging groups. The vinylene shifts should increase as the electronic symmetry of the dye increases, tending toward 100 nm. In fact, the introduction of bridging groups in pyrylothiacyanines (dyes IX-XII), in which the pyran residue is less basic, leads to an increase in the vinylene shift, whereas their introduction in pyridocyanines (dyes XIII, XIV, XIX, and XX), in which the pyridine system is more basic even without such introduction, leads to a decrease in the vinylene shift. The width of the absorption bands of slightly asymmetrical dyes, as in the case of symmetrical dyes, should decrease as the polymethine chain becomes longer, whereas it should increase in the case of markedly asymmetrical dyes [4]. In fact, contraction of the bands is observed as the polymethine chain becomes longer in pyrylocyanines V-XII, the molecules of which are relatively slightly asymmetrical; the effect is greater for the less asymmetrical pyrolo(indo)cyanines. The regularity is reversed in the case of pyridocyanines XIII-XX, which have considerably greater electronic asymmetry as compared with pyrylocyanines: the bands become wider as the polymethine chain is made longer. It is important that the observed effect is greater in both series of compounds for dyes with trimethylene bridges.

Thus it may be concluded that in the examined dyes the trimethylene groupings increase the electron-donor character of the heterocyclic residues more markedly than the ethylene groupings. Although there should not be a direct relationship between the electron-donor character of the indicated residues in the dyes and the basicities of the heterocycles themselves, a six-membered hydrocarbon ring annelated in the 2 and 3 positions relative to the pyridine ring also increases the basicity of the latter to a greater degree than a five-membered ring [5].

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*See [1] for the symmetrical dyes.

In conclusion, let us note that the absorption bands of the examined pyrylocyanines with cyclic groupings, as in the case of the corresponding symmetrical dyes, have more resolved fine structures than the absorption bands of their unsubstituted analogs. This effect is expressed quantitatively in an increase in the coefficients of the fine structure (F), symbatically with respect to which the coefficients of asymmetry ($\gamma_1$) and excess ($\gamma_2$) also increase. In contrast to the symmetrical pyridocyanines, in the series of examined unsymmetrical pyridocyanines the observed regularity is reversed — cyclic groupings lead to a decrease in the coefficient of the fine structure.

## EXPERIMENTAL

The absorption spectra were determined with an SF-4A spectrophotometer and were processed as in [1]. The purity of the preparations was monitored by thin-layered chromatography (TLC) on Silufol UV-254 plates (elution with acetonitrile).

2,4-Diphenyl-7-ethoxymethylene-5,7-dihydrocyclopenta[b]pyrylium Perchlorate (I). A mixture of 0.74 g (2 mmole) of 2,4-diphenyl-5,6-dihydrocyclopenta[b]pyrylium perchlorate [6] and 0.40 g (2.4 mmole) of ethyl orthoformate in 5 ml of acetic anhydride was refluxed for 20 min. Perchlorate I was purified by recrystallization from acetic acid (Table 2).

1,3,3-Trimethyl-2-{2-(2,4-diphenyl-5,6-dihydrocyclopenta[b]pyran-7-yl)-vinyl}-3H-indolium Perchlorate (V). A mixture of 0.107 g (0.25 mmole) of perchlorate I, 0.068 g (0.25 mmole) of 1,2,3,3-tetramethylindolinium perchlorate, and 0.021 g (0.25 mmole) of anhydrous sodium acetate was heated in 3 ml of a mixture of acetic anhydride and acetic acid (1:1) at 125°C for 15 min. The product was purified by washing with acetic acid, benzene, and ether.

1,3,3-Trimethyl-2-{4-(2,4-diphenyl-5,6-dihydrocyclopenta[b]pyran-7-yl)-1,3-butadienyl}-3H-indolium Perchorate (VI). A mixture of 0.225 g (0.5 mmole) of perchlorate II, which was obtained in the same way as IV by the method in [2] and was not isolated in analytically pure state, and 0.13 g (0.5 mmole) of 1,2,3,3-tetramethylindolinium perchlorate in 3 ml of acetic anhydride containing several drops of pyridine was refluxed for 5 min. The mixture was then chromatographed on aluminum oxide (elution with acetonitrile), after which the product was precipitated from acetonitrile by the addition of an aqueous solution of sodium perchlorate. The product was purified by recrystallization from a mixture of acetic acid with acetonitrile (1:1).

3-Ethyl-2-{2-(2,4-diphenyl-5,6-dihydrocyclopenta[b]pyran-7-yl)vinyl}-benzothiazolium Perchlorate (IX). This compound was obtained from perchlorate I and 2-methyl-3-ethylbenzothiazolium toluenesulfonate by the method used to prepare VI. The mixture was chromatographed and the product was reprecipitated from acetonitrile with 30% $HClO_4$ and recrystallized from acetic acid.

3-Ethyl-2-{4-(2,4-diphenyl-5,6-dihydrocyclopenta[b]pyran-7-yl)-1,3-butadienyl}benzothiazolium Perchlorate (X). This compound was obtained and purified in the same way as VI using perchlorate II and 2-methyl-3-ethylbenzothiazolium toluenesulfonate.

1-Methyl-2,4-diphenyl-7-[2-(1,3,3-trimethylindolin-2-ylidene)vinyl]-5,6-dihydrocyclopenta[b]pyridinium Perchlorate (XIII). A mixture of 0.277 g (0.5 mole) of pyrylocyanine V and 1 ml (2.5 mmole) of a 7.5% methanol solution of methylamine in 2 ml of acetonitrile was maintained at 20°C for 30 min. Dye XIII was precipitated with an aqueous solution of sodium perchlorate, chromatographed on aluminum oxide (elution with acetonitrile), and recrystallized from alcohol.

Pyridocyanines XIV, XVII, and XVIII. These compounds were obtained from the corresponding pyrylocyanines VI, IX, and X by the method used to prepare XIII.

1-Methyl-2,4-diphenyl-8-[2-(1,3,3-trimethylindolin-2-ylidene)vinyl]-5,6,7,8-tetrahydroquinolinium Perchlorate (XV). This compound was obtained in the same way as XIII with heating at 50°C for 15 min using pyrylocyanine VII.

Pyridocyanines XVI, XIX, and XX. These compounds were obtained in the same way as dye XV from the corresponding pyrylocyanines (VIII, XI, and XII). The pyridocyanines obtained were recrystallized from alcohol, while dyes XVIII and XX were recrystallized from a mixture of alcohol and acetonitrile (2:1).

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# HYDROGENATION OF OXYGEN-CONTAINING HETEROCYCLIC COMPOUNDS ON GROUP VIII METALS

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The hydrogenation of a number of oxygen-containing heterocyclic compounds on Pt, Pd, and Rh blacks in the liquid phase at atmospheric pressure was investigated. The results are compared with data on H–D exchange with $D_2O$ and are interpreted from the point of view of the theory of $\pi$-complex adsorption.

We have previously reported the hydrogenation and H–D exchange of benzofuran and its alkyl derivatives on group VIII metals [1-3]. In the present research we investigated the hydrogenation of a number of oxygen-containing heterocycles under mild conditions in the presence of Pt, Pd, and Rh blacks. The results are presented in Tables 1 and 2.

It is apparent from Table 1 that the reaction proceeded selectively in the hydrogenation of benzofuran in the presence of Pd and Rh: the $C_2$–$C_3$ bond was hydrogenated to give 2,3-dihydrobenzofuran. In addition to this process, hydrogenolysis of the O–$C_2$ bond occurred in the presence of Pt. As a result, phenols are present along with 2,3-dihydrobenzofuran in the reaction products. With respect to their activity* in the investigated reaction the metals can be arranged in the order Pd > Rh > Pt. It should be noted that the most active catalyst, viz., Pd, upon storage in air retains approximately the same activity for 10 days after its preparation; its activity decreases only after this period. When Pd upon which hydrogenation has already been accomplished was used again, the activity of the catalyst was also quite high in the hydrogenation of benzofuran (Table 1).

With respect to their reactivities in hydrogenation (see Table 2) the investigated benzofurans can be arranged in the order benzofuran > 2-methylbenzofuran > 2-ethylbenzofuran > 2-propylbenzofuran. Thus alkyl substituents retard the hydrogenation of benzofurans on Pd, evidently due to steric hindrance vis-à-vis $\pi$-complex adsorption. It is apparent from Table 2 that the nature of the substituent in the heteroring also affects the rate of hydrogenation.

The results obtained in a study of H–D exchange of the investigated heterocycles [2, 3] make it possible to explain the principles of hydrogenation of these compounds and to examine them from the point of view of the theory of $\pi$-complex adsorption [4], according to which the first step in the catalytic reaction of aromatic and unsaturated compounds on transition metals is the formation of a surface $\pi$ complex. In the case of complex molecules their various fragments may make different contributions to the interaction with the catalyst [2, 3, 5], which affects the orientation of the molecule on the surface and the reaction pathway as a

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*By activity here we have in mind the amount of hydrogen absorbed per unit time at the start of the reaction relative to the area of the catalyst.

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