

## PYRYLOCYANINES.

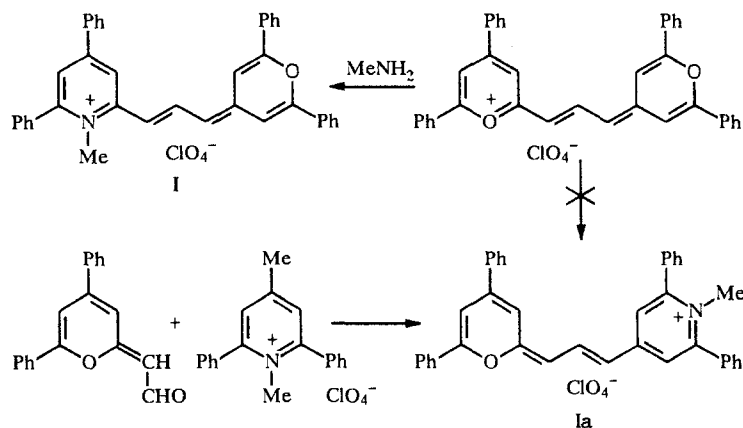
### 30.\* UNSYMMETRICAL 4,6,4',6'-TETRAPHENYL-SUBSTITUTED 2-PYRIDO-2-PYRYLOCYANINES WITH TRIMETHYLENE GROUPINGS IN THE CHROMOPHORE

N. A. Derevyanko, A. A. Ishchenko,  
and A. I. Tolmachev

*The reaction of methylamine with symmetrical 4,6,4',6'-tetraphenyl-substituted 2-pyrylopolycarbocyanines, in which both  $\alpha$  positions of the polymethine chain are linked to the  $\beta$  positions of the heterocyclic residues by trimethylene groups, was used to synthesize the corresponding pyridopyrylocyanines. The effect of trimethylene groupings in the 2-pyridocyanines on this transformation was examined. The principles involved in the color of the synthesized pyridopyrylocyanines were studied.*

It has been previously shown that the oxygen atoms in pyrylocyanines are easily replaced by an  $\text{NCH}_3$  group by the action of methylamine on them [2]. In the 4-pyrylocyanine series both unsymmetrical pyridopyrylocyanines and symmetrical pyridocyanines can be obtained by means of this reaction [2]. In the isomeric  $\alpha$  series replacement of the oxygen atoms by an  $\text{NCH}_3$  group proceeds so readily that only symmetrical pyridocyanines can be isolated [3].

The reaction of a tetraphenyl-substituted 2-pyrylo-4-pyrylocarbocyanine [4] with methylamine provides particularly clear evidence for the greater ease of nucleophilic substitution in the 2-pyrylocyanine series as compared with the corresponding 4-substituted isomers.



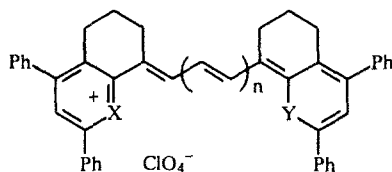
Of the two possible unsymmetrical dyes I and Ia, only 2-pyrido-4-pyrylocarbocyanine I is formed, which is indicated unambiguously by the fact that it absorbs in a shorter-wavelength region of the spectrum ( $\lambda_{\text{max}} = 565 \text{ nm}$  in  $\text{CH}_2\text{Cl}_2$  and  $538 \text{ nm}$  in  $\text{CH}_3\text{CN}$ ) than the isomeric tetraphenyl-substituted 4-pyrido-4-pyrylocarbocyanine [2] ( $\lambda_{\text{max}} = 578 \text{ nm}$  in  $\text{CH}_2\text{Cl}_2$  and  $550 \text{ nm}$  in  $\text{CH}_3\text{CN}$ ). Proceeding from the fact that the carbon-carbon bonds of the  $\alpha$ -pyrylium residue participate to a

\*See [1] for Communication 29.

significantly greater extent in the overall conjugation system than in the corresponding pyridinium ring [3, 4], dye Ia should absorb in a longer-wavelength region as compared with the above-mentioned 4-pyrido-4-pyrylocarbocyanine. Attempts to synthesize and isolate this compound in the individual state were unsuccessful. We were able to obtain it only qualitatively by condensation of 2-formylmethylene-4,6-diphenyl-2(H)-pyran [5] with 1,4-dimethyl-2,6-diphenylpyridinium perchlorate in the presence of sodium hexamethyldisilylamide and were able to record the corresponding spectrum, the data from which ( $\lambda_{\max} = 609 \text{ nm}$  in  $\text{CH}_2\text{Cl}_2$  and  $581 \text{ nm}$  in  $\text{CH}_3\text{CN}$ ) confirmed the correctness of the conclusions drawn above.

In the present research we were able to obtain the first representatives of pyridopyrylocyanines of the  $\alpha$  series II-IV in good yields by the action of an excess amount of a methanol solution of methylamine on solutions of the corresponding symmetrical pyrylocyanines V-VII [6] in acetonitrile.

The previously undescribed symmetrical pyridocyanine X was also synthesized by heating dye VII with methylamine in DMSO. Dyes VIII and IX were described in [6].



II - X

II-IV X=NCH<sub>3</sub>; Y=O; V-VII X=Y=O; VIII-X X=Y=NCH<sub>3</sub>; II, V, VII n=0; III, VI, IX n=1;  
IV, VII, X n=2

Among the spectral characteristics of solutions of dyes II-X in the slightly polar methylene chloride and in the highly polar acetonitrile, in addition to  $\lambda_{\max}$  and  $\log \epsilon$ , the mean positions of the bands  $M^{-1}$  determined by the method of moments, the oscillator forces  $f$ , and the band widths  $\delta$  are presented in Table 1. Table 1 also contains deviations  $D_\lambda$  and  $D_M$  calculated, respectively, from the  $\lambda_{\max}$  and  $M^{-1}$  values.

It is apparent from Table 1 that pyridopyrylocyanines II-IV absorb in a significantly shorter-wavelength region of the spectrum than the corresponding symmetrical pyrylo- and pyridocyanines and not in the region between them, as one might have expected from the different participation of the C—C bonds of  $\alpha$ -pyrylium and pyridinium heteroresidues in conjugation [3, 4]. Such a strong hypsochromic shift of  $\lambda_{\max}$  and  $M^{-1}$  of unsymmetrical dyes II-IV as compared with symmetrical dyes (V-X) is the result of their pronounced electronic asymmetry. Evidence for this is provided for the larger deviations, which exceed the analogous values of the heretofore known unsymmetrical cyanines with the same length of the polymethine chain [2, 7].

The electronic asymmetry of dyes II-IV increases regularly with lengthening of the chain, as indicated by the increase in the  $D_\lambda$  and  $D_M$  values (see Table 1).

In contrast to the corresponding symmetrical dyes, the vinylenic shifts for the investigated pyridopyrylocyanines attenuate markedly. Thus passing from dicarbocyanine III to tricarbocyanine IV in solution in methylene chloride is accompanied by deepening of the color by only 19 nm with respect to  $\lambda_{\max}$  and by 33.1 nm with respect to  $M^{-1}$ , whereas in the case of solutions in acetonitrile one even observes a hypsochromic shift of  $\lambda_{\max}$  and  $M^{-1}$  by 7.0 and 8.3 nm, respectively. These data provide evidence that pronounced alternation of the orders of the bonds in the chromophore, which is close in magnitude to that observed for typical carotinoids, occurs in the case of pyridopyrylocyanines II-IV. As in the case of typical carotinoids, rather small extinctions and oscillator forces and extremely broad absorption bands are characteristic for the investigated unsymmetrical dyes. The  $\epsilon$  values are much smaller and the  $\delta$  values are substantially larger for pyridopyrylocyanines II-IV than for symmetrical cyanines V-X.

Replacement of methylene chloride by acetonitrile leads to hypsochromic shifts, a decrease in the intensities, and broadening of the bands in the case of the unsymmetrical dyes. These effects increase regularly with lengthening of the polymethine chain.

In the case of the unsymmetrical dyes the positive charge is shifted primarily to the ring with greater electron-donor character [7, 8]. The charges of the pyridinium ring should therefore primarily undergo nucleophilic solvation. This in turn will give rise to an increase in its electron-donor character (an increase in the electronic asymmetry of the dye) [7, 8], which is also manifested in an increase in the  $D_\lambda$  and  $D_M$  values, the hypsochromic shifts, and the widths of the bands and a decrease

TABLE 1. Spectral Characteristics of Dyes II-X

Com- pound	Solvent	$\lambda_{\max}$ , nm	$D\lambda$ , nm ( $\text{cm}^{-1}$ )	$\lg \epsilon$	$f$	$M^{-1}$ , nm	$D_M$ , nm ( $\text{cm}^{-1}$ )	$\sigma$ , $\text{cm}^{-1}$
II	CH <sub>2</sub> Cl <sub>2</sub>	615	159,5 (3265)	4,31	0,57	579,2	147,3 (3420)	2090
	CH <sub>3</sub> CN	565	195 (4430)	4,15	0,55	533,7	173,6 (4492)	2410
III	CH <sub>2</sub> Cl <sub>2</sub>	655	221 (3790)	4,51	0,81	618,3	202,2 (3935)	2200
	CH <sub>3</sub> CN	592	270 (5220)	4,44	0,84	561,3	226,0 (5037)	2610
IV	CH <sub>2</sub> Cl <sub>2</sub>	674	311 (4645)	4,57	0,92	651,4	260,6 (4340)	2300
	CH <sub>3</sub> CN	585	374 (6600)	4,53	1,02	553,2	282 (6048)	2850
V	CH <sub>2</sub> Cl <sub>2</sub>	835	—	4,79	0,51	781,9	—	1146
	CH <sub>3</sub> CN	830	—	4,72	0,53	768,3	—	1236
VI	CH <sub>2</sub> Cl <sub>2</sub>	940	—	5,14	0,96	874,4	—	1071
	CH <sub>3</sub> CN	930	—	4,96	0,87	848,3	—	1241
VII	CH <sub>2</sub> Cl <sub>2</sub>	1050	—	5,20	1,07	971,9	—	1022
	CH <sub>3</sub> CN	1033	—	4,91	1,10	892,1	—	1756
VIII	CH <sub>2</sub> Cl <sub>2</sub>	714	—	4,40	0,30	671,1	—	1430
	CH <sub>3</sub> CN	690	—	4,50	0,52	646,2	—	1650
IX	CH <sub>2</sub> Cl <sub>2</sub>	812	—	4,77	0,53	766,8	—	1180
	CH <sub>3</sub> CN	794	—	4,68	0,67	726,2	—	1540
X	CH <sub>2</sub> Cl <sub>2</sub>	920	—	4,12	—	852,1	—	1290
	CH <sub>3</sub> CN	885	—	—	—	778,3	—	2300

in the intensities and attenuation of the vinylene shifts on passing from methylene chloride to the more nucleophilic acetonitrile (see Table 1).

The trimethylene groupings have electron-donor properties. Their introduction into odd-numbered positions of the chromophore with respect to the heteroatom should therefore lead to a decrease in the magnitudes of the positive charges [9]. In fact, this is manifested distinctly in weakening of the nucleophilic solvation of dyes V-VII as compared with their analogs without cyclic groupings [3, 4]. Thus replacement of methylene chloride by the more nucleophilic acetonitrile gives rise to hypsochromic shifts of  $\lambda_{\max}$  and  $M^{-1}$  and broadening of the bands of pyryloxyanines V and VI by, respectively, 70, 227, 90  $\text{cm}^{-1}$  and 110, 352, 170  $\text{cm}^{-1}$  (see Table 1), as compared with 158, 337, 103  $\text{cm}^{-1}$  and 184, 423, 191  $\text{cm}^{-1}$  for their analogs [3, 4].

The decrease in the magnitudes of the positive charges in the heteroresidues of pyryloxyanines V-VII due to the introduction of saturated cyclic groupings into the chromophore also decreases the activity of their heteroresidues with respect to nucleophilic agents, which is one of the factors that made it possible to obtain pyridopyryloxyanines II-IV of the  $\alpha$  series. Under the same conditions analogs of dyes V-VII without these groupings form symmetrical pyridoxyanines on reaction with methylamine [3].

## EXPERIMENTAL

The absorption spectra of solutions of the compounds in purified acetonitrile and methylene chloride stabilized with 1% absolute ethanol were recorded with a Specord M 40 spectrophotometer. The purity of the preparations was monitored by TLC on Silufol-254 plates by elution with acetonitrile.

The results of elementary analysis for C, H, and Cl were in agreement with the calculated values.

**1-Methyl-4,6-diphenyl-2-[3-(2,6-diphenylpyran-4-ylidene)-2-propen-1-ylidene]pyridinium Perchlorate (I, C<sub>38</sub>H<sub>30</sub>NClO<sub>5</sub>).** This compound was obtained by the reaction of 0.15 g (0.248 mmole) of 4,6-diphenyl-2-[3-(2,6-diphenylpyran-4-ylidene)-2-propen-1-ylidene]pyrylium perchlorate in 5 ml of acetonitrile with 1.5 ml of a 7.5% methanol solution of methylamine at  $20 \pm 2^\circ\text{C}$  for 0.5 h. The dye precipitated from the reaction mixture and had mp 216-217°C. The yield was 0.09 g (58%).

**1-Methyl-2,4-diphenyl-8-[(2,4-diphenyl-6,7-dihydro-5H-1-benzopyran-8-ylidene)methylidene]-5,6,7,8-tetrahydroquinolinium Perchlorate (II, C<sub>44</sub>H<sub>38</sub>NClO<sub>5</sub>).** A suspension of 0.228 g (0.33 mmole) of pyryloxyanine V in 2 ml of acetonitrile was heated with a fivefold excess of a methanol solution of methylamine at 40°C for 0.5 h. The dye was

precipitated with saturated aqueous sodium perchlorate solution and had mp 231-232°C (from ethanol). The yield was 0.196 g (85%).

**1-Methyl-2,4-diphenyl-8-[3-(2,4-diphenyl-6,7-dihydro-5H-1-benzopyran-8-yl)-2-propen-1-ylidene]-5,6,7,8-tetrahydroquinolinium Perchlorate (III, C<sub>46</sub>H<sub>40</sub>NClO<sub>5</sub>).** This compound was obtained in the same way as dye II from 0.18 g (0.254 mmole) of symmetrical pyrylocyanine VI by heating at 40-50°C for 0.5 h and had mp 220-222°C (from ethanol). The yield was 0.164 g (90%).

**1-Methyl-2,4-diphenyl-8-[5-(2,4-diphenyl-6,7-dihydro-5H-1-benzopyran-8-ylidene)-1,3-pentadien-1-ylidene]-5,6,7,8-tetrahydroquinolinium Perchlorate (IV, C<sub>48</sub>H<sub>42</sub>NClO<sub>5</sub>).** This compound was obtained in the same way as II using pyrylocyanine VII by heating at 80°C for 0.5 h. The reaction of 0.17 g (0.22 mmole) of VII yielded 0.13 g (76%) of pyridopyrylocyanine with mp 188-189°C.

**1-Methyl-2,4-diphenyl-8-[5-(1-methyl-2,4-diphenyl-6,7-dihydro-5H-quinolin-8-yl)-1,3-pentadien-1-ylidene]-5,6,7,8-tetrahydroquinolinium Perchlorate (X, C<sub>49</sub>H<sub>45</sub>N<sub>2</sub>ClO<sub>4</sub>).** A suspension of 0.15 g (0.2 mmole) of pyrylocyanine VII in 2 ml of a 7.5% solution of methylamine in DMSO was heated at 85-90°C for 0.5 h. The dye was precipitated with saturated aqueous sodium perchlorate solution and had mp 152-154°C. The yield was 0.095 g (61%).

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