

Reactions with Methylamine of Pyrilo-2-cyanines Containing Polyfluorophenyl Substituents

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Abstract—Reactions of symmetric and unsymmetrical pyrilo-2-cyanines containing polyfluorophenyl substituents with methylamine give rise to the corresponding pyridocyanines, 1,3-cyclohexadiene derivatives, or 1-methyl-2-pyridone. The type of the reaction product depends on the structure of the initial dye and the reaction conditions.

Polymethine dyes (PMD) are widely used in the modern phototechnology [1]. Due to their strong and selective absorption characteristics these substances found successful application as sensitizers and components of laser media in the longwave visible and near infrared region. Their color and useful properties depend on the special features of their structure and to a large measure on the character of the substituents in the terminal groups of the polymethine chain. For instance, the data on effect and fluoroalkyl groups on the spectral, physicochemical, and photographic characteristics of PMD were compiled in [2].

We formerly performed the first synthesis of pyrilium **I**, **II** and N-methylpyridinium **III**, **IV** salts containing in the ring a polyfluoroaryl group and active methyl or methylene group and demonstrated the possibility to prepare pyrilo-2-cyanines with polyfluoroaryl substituents attached to heterocycles [3–6]. The pyrilocyanines are known to readily react with methylamine with oxygen replacement by an MeN group providing a convenient route to the corresponding pyridinium dyes [7–10]. Aiming at preparation of new polymethine dyes in this study we investigated the reaction with methylamine of polyfluorophenyl-containing pyrilocyanines (styryls and symmetric dyes).

Initial styryls **Va**, **b**, and **VI** were prepared reacting pyrilium salts **I** and **II** [4] with *p*-dimethylaminobenzaldehyde **VII** in Ac₂O [3]. It was established that heating of dyes **Va**, **b** with methylamine in a mixture EtOH–DMSO resulted in replacement of the ring oxygen by

MeN group, and in the case of initial styryl **Va** in substitution of the *p*-fluorine of the pentafluorophenyl fragment by a methylamino group. Therewith dyes **VIIIa**, **b** were formed (Scheme 1).

In a reaction mixture obtained under the same conditions from compound **VI** and methylamine styryl **IX** was detected in trace amounts. The main reaction product according to spectral and analytical data was 1,3-cyclohexadiene derivative **X** (yield 80%) (Scheme 2). Its formation in all likelihood involves a reagent attack on the 2 position of the pyrilium ring of molecule **VI** followed by recyclization with participation of the *exo*-ethylene bond (cf. [11]).

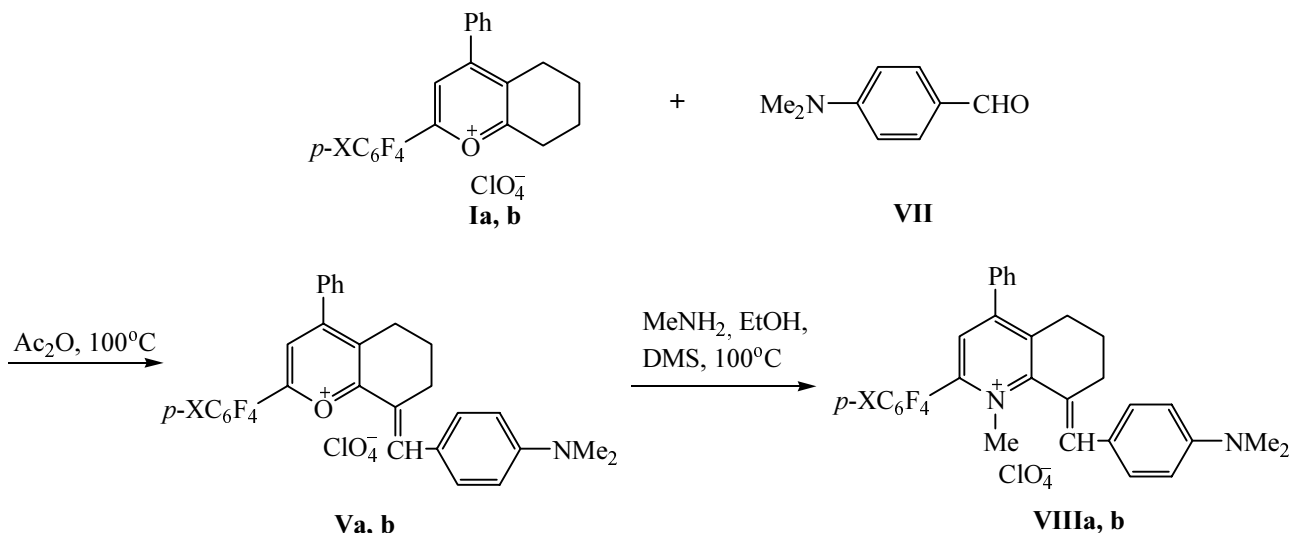
The different reactivity of compounds **VI** and **Va**, **b** might originate from higher sterical requirements in the polymethylene ring of tetrahydrobenzopyrilocyanines hampering the recyclization.

Dye **IX** was prepared by an independent synthesis from aldehyde **VII** and pyridinium salt **III**, obtained by procedure [5]. Yet the reaction of aldehyde **VII** with 1-methyl-2-pentafluorophenyl-4-phenyl-5,6,7,8-tetrahydro-1-quinolinium perchlorate **IV** did not result in styryl of type **VIII**. This fact is consistent with the data of [12] where similar difficulties have been met in an analogous reaction of 1-methyl-2,4-diphenyltetrahydroquinolinium salt.

Symmetric pyrilocyanines **XIa**, **b** [3, 5] readily react with 10% ethanol solution of methylamine with replacement of one oxygen atom (cf. [10]) affording the corresponding pyridopyrilocyanines **XIIa**, **b**. The reaction carried out in the EtOH–DMSO mixture gives rise to expected [9] symmetric pyridocyanines of **XIIIa**, **b** type;

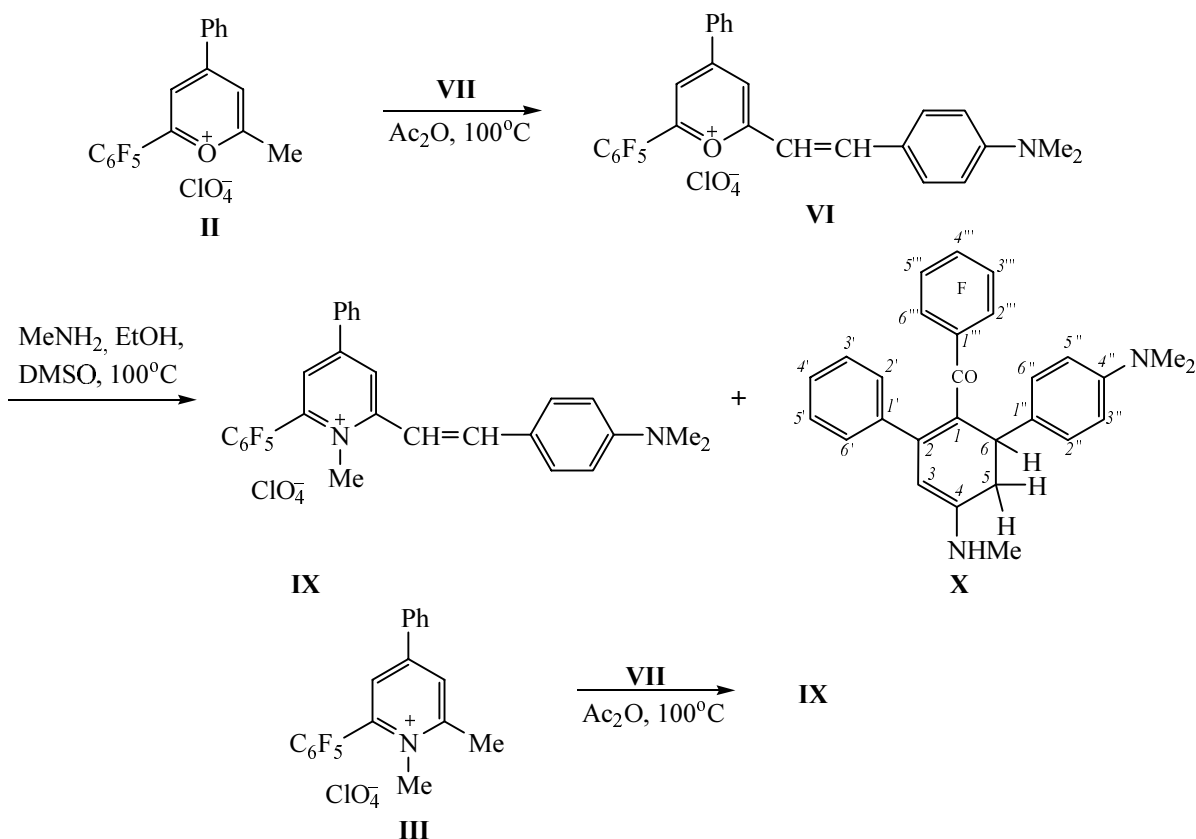
[†] Deceased.

Scheme 1.



I, V, X = F (a), OMe (b); VIII, X = NHMe (a), OMe (b).

Scheme 2.

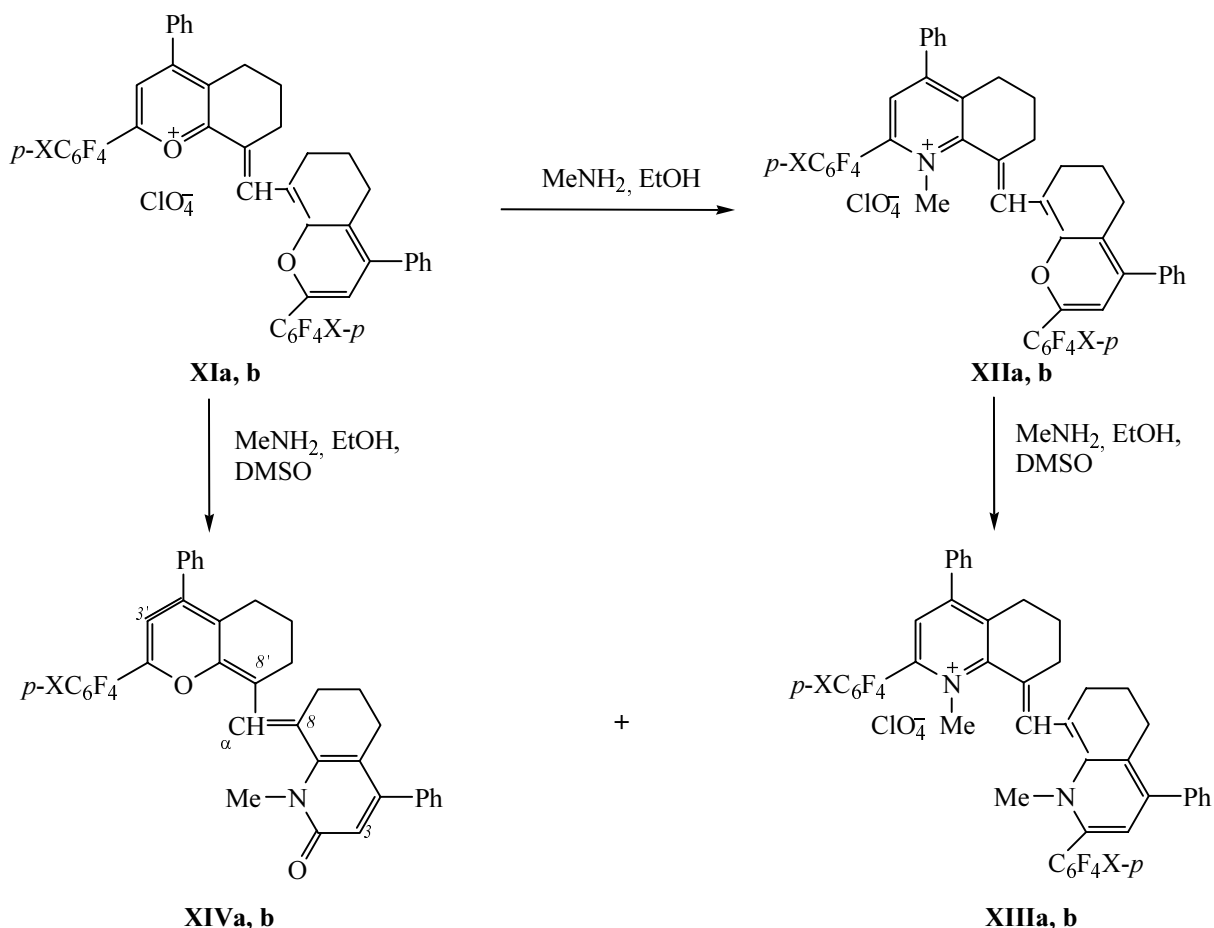


however the main reaction products are neutral compounds that on the force of IR and ^1H NMR spectra has been assigned structures of 2-pyridones **XIVa, b**. Two-stage synthesis of dyes **XIIIa, b** proved to be more efficient when first pyridopyrilonium **XIIa, b** were

obtained that treated with methylamine in the EtOH–DMSO mixture afforded the target products in 50–60% yield (Scheme 3).

The composition and structure of compounds synthesized are consistent with the data of elemental

Scheme 3.



XI, $\text{X} = \text{F}$ (a), OMe (b); **XII–XIV**, $\text{X} = \text{MeNH}$ (a), OMe (b).

analysis, molecular mass values determined by the high resolution mass spectrometry, and with the spectral characteristics. For instance, the ^{19}F NMR spectrum of compound **X** confirms the presence in the molecule of a pentafluorophenyl moiety. In the IR spectrum the absorption bands are observed of NHMe group at 3446 cm^{-1} and of a carbonyl conjugated with an α,β -unsaturated system containing at the end of the conjugation chain a donor substituent (1612 cm^{-1} , cf. [14]). The presence of a carbonyl is also proved by the signal of a carbon atom belonging thereto in the ^{13}C NMR spectrum at 179.77 ppm . The ^1H NMR spectrum is in agreement with the assumed structure. A doublet at 2.67 ppm ($J 5.5\text{ Hz}$) and a broadened singlet centered at 5.27 ppm belong to the NHMe group, a singlet at 4.79 ppm to methine proton in position 3. Signals at 2.41 , 3.10 , and 4.48 ppm involved into an ACX system evidence a presence in the molecule of three mutually coupled aliphatic protons. A doublet of doublets at 3.10 ppm

originating from geminal ($J 16\text{ Hz}$) and vicinal ($J 7\text{ Hz}$) couplings likely corresponds to one of H^5 protons. Doublets at 2.41 ppm ($J 16\text{ Hz}$) and 4.48 ppm ($J 7\text{ Hz}$) may be assigned to the second proton in position 5 and to proton H^6 respectively. The structure of compound **X** is additionally confirmed by the data of the ^{13}C NMR spectrum and of two-dimensional correlation spectrum $^{13}\text{C}\text{-}^1\text{H}$ (COSY) that reveals the bonding of alicyclic protons to the carbon atoms C^5 and C^6 .

The value of molecular mass for compound **XIVa** measured on high resolution mass spectrometer corresponded to its assumed structure. The IR spectra contain absorption bands in the region of vibrations belonging to the polyfluorinated aromatic ring, and also to the stretching vibrations of carbonyl and NH group. The character of ^{19}F and ^1H NMR spectra containing two sets of the like signals in the intensity ratio 4:3 suggests the presence of two isomers of pyridone **XIVa**. For instance, in the ^{19}F NMR spectrum appear signals from

Table 1. Yields, melting points, absorption bands in longwve region, and elemental analyses of dyes **Va, b, VI, VIIIa, b, IX, XIIa, b, XIIIa, b, and XVa–c, d**

Compd. no.	Yield, %	mp (decomp.), °C	λ_{\max} , nm (log ϵ)	Found, %					Formula	Calculated, %				
				C	H	Cl	F	N		C	H	Cl	F	N
Va	64	215–217	691 (4.76)	59.04	3.54	5.90	16.01	2.31	C ₃₀ H ₂₃ ClF ₅ NO ₅	59.27	3.81	5.83	15.63	2.30
Vb	80	213–216	690 (4.75)	60.06	4.26	5.80	12.38	2.39	C ₃₁ H ₂₆ ClF ₄ NO ₆	60.05	4.23	5.71	12.26	2.26
VI	62	233–234	692 (4.79)	56.92	3.43	6.60	16.67	2.50	C ₂₇ H ₁₉ ClF ₅ NO ₅	57.10	3.37	6.24	16.73	2.46
VIIIa	60	146–147	502 (4.26)	60.45	4.84	6.09	12.40	6.68	C ₃₂ H ₃₀ ClF ₄ N ₂ O ₄	60.81	4.78	5.61	12.02	6.65
VIIIb	40	178–182	508 (4.40)	60.40	4.60	6.19	12.02	4.42	C ₃₂ H ₂₉ ClF ₄ N ₂ O ₅	60.71	4.62	5.60	12.01	4.42
IX	62	288–290	543 (4.67)	57.85	3.90	6.30	16.44	4.68	C ₂₈ H ₂₂ ClF ₅ N ₂ O ₄	57.89	3.82	6.10	16.35	4.82
XIIa	58	168–172	608 (4.22)	61.67	4.17	3.81	16.56	4.55	C ₄₆ H ₃₆ ClF ₈ N ₃ O ₅	61.51	4.04	3.95	16.92	4.68
XIIb	84	161–165	602 (4.25)	61.07	3.86	–	16.76	1.65	C ₄₆ H ₃₄ ClF ₈ NO ₇	61.37	3.81	–	16.88	1.55
XIIIa	66	174	727 (4.60)	62.33	4.44	3.96	–	6.06	C ₄₇ H ₃₉ ClF ₈ N ₄ O ₄	61.94	4.31	3.89	16.68	6.15
XIIIb	45	164	673 (4.37) 728 (4.57)	61.67	4.22	3.50	–	2.95	C ₄₇ H ₃₇ ClF ₅ N ₂ O ₇	61.81	4.08	3.88	16.64	3.07
XVa		301–303 (280–28 [16]) ^a	672 (4.73) (Cp.[15])											
XVb		240–242 (241–242 [17]) ^a	513 (4.44)											
XVc		227–230 (233 [18]) ^a	679 (4.79)											
XVd	79	146–148	486 (4.37)	69.94	5.87	6.70	–	5.16	C ₃₁ H ₃₁ ClN ₂ O ₄	70.11	5.88	6.68	–	5.28

^aPublished values of melting points are given in parentheses.

two *para*-substituted tetrafluorophenyl groups. In the ¹H NMR spectrum compound **XIVa** gave rise to multiplets of alicyclic protons in the region 1.45–2.67 ppm, two broadened singlets at 3.10 and 3.14 ppm (the protons of NHMe group), two singlets at 3.53 and 3.68 ppm (the protons of Me group at heterocyclic nitrogen atom), and three pairs of singlets in the region 5.81–6.76 ppm belonging to protons H³, H^{3'}, and H^α attached to unsaturated carbon atoms. The signals of two phenyl groups appear in the region 7.18–7.45 ppm, and the broadened singlet of NH group at 4.05 ppm.

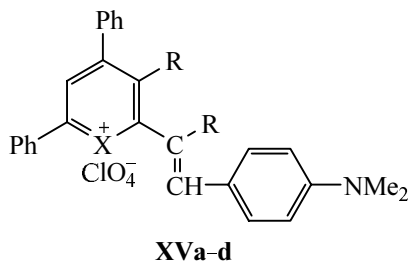
The registering of NMR spectra at 110°C did not lead to broadening and coalescence of pairs of signals thus excluding the presence of conformational isomers. The *E,Z*-isomerism of the molecule with respect to the double bond C^α=C^δ seems more probable. The calculation of simplified models for both possible structures by MM⁺ method showed that the planes of the heterocyclic

systems of pyran and pyridine formed a dihedral angle of 110° in *E*-isomer and of 134° in *Z*-isomer. The spatial distance between H^α protons and NMe group was 2.47 and 3.36 Å respectively. Inasmuch as the nuclear Overhauser effect revealed the through-space coupling of these protons in the minor component of the mixture, the latter was assigned *E*-structure. A similar pattern of NMR spectra was observed for compound **XIVb**.

We investigated formerly the electron absorption spectra of polyfluorophenyl-substituted pyrilo-2-cyanines, and in particular an effect on the spectral characteristics of dyes was analyzed produced by replacement of phenyl groups by pentafluorophenyl ones [6]. In the present study we compared the absorption spectra of newly synthesized dyes **XIIa, b** and **XIIIa, b** with the spectra of unfluorinated polycyanines.

It turned out that the replacement of the phenyl group by polyfluorophenyl one caused a small blue shift ($d \leq$

15 nm) in compounds **XIIa, b** and a red shift of the long-wave band in compounds **XIIIa, b**. The changes in absorption spectra due to the heterocycle transformation were in the expected range [10]. In going from pyrilo-cyanines **XIa, b** [6] to pyridopyrilo- and pyridocyanines **XIIa, b** and **XIIIa, b** a significant blue shift of the longwave maximum is observed, and the largest effect (over 200 nm, cf.[10]) occurs when a single oxygen is substituted by NMe group.



The published electronic spectra of unfluorinated analogs **XVa-d** of the synthesized dyes were registered in different solvents and were uncomparable. Therefore we prepared styryls **XVa-d** by known procedures and recorded their spectra in CH_2Cl_2 (Table 1). In the spectra of dyes **Va, b, VI, VIIIa, b, and IX**, as also in the spectra of unfluorinated analogs (cf. [14]) the longwave maximum appears as a broad strong absorption band shifted by 11–30 nm to shorter waves with respect to the corresponding dye of **XV** type. As seen, introduction into the *para*-position of the polyfluorophenyl ring of styryl **V** of a donor methoxy group did not result in a deeper color (cf. [6]).

Yields, melting points, elemental analysis, and absorption spectra of dyes **Va, b, VI, VIIIa, b, IX, XIIa, b, and XIIIa, b** are given in Table 1, data of ^1H and ^{19}F NMR spectra in Table 2.

EXPERIMENTAL

Electron absorption spectra were recorded on spectrometers Specord UV-VIS, Specord M-40, and Beckman DU-8 (further in the text are given the absorption bands of longwave region). IR spectra were measured on spectrophotometer UR-20 from solutions in CHCl_3 . ^1H , ^{13}C , and ^{19}F NMR spectra were registered from CDCl_3 solutions on spectrometers Bruker AC-200, Bruker WP-200SY, and DRX-500 using HMDS, CHCl_3 , and C_6F_6 as internal references. Mass spectra were taken on Finnigan MAT 8200 instrument at ionizing electrons energy 70 eV.

The column chromatography was performed on aluminum oxide of the II grade activity. The solvent ratios in mixtures are reported by volume.

8-[(*p*-Dimethylaminophenyl)ethenyl]-2-(*p*-X-tetrafluorophenyl)-4-phenyl-5,6,7,8-tetrahydro-1-benzopyrilium (Va, b) and 2-[(*p*-dimethylaminophenyl)ethenyl]-4-phenyl-6-pentafluorophenylpyrilium (VI) perchlorates. A mixture of 1 mmol of pyrilium salt **Ia, b, II**, 1 mmol of benzaldehyde **VII** and 2 ml of Ac_2O was heated for 30 min at 90–100°C. On cooling the reaction mixture was poured into 25 ml of Et_2O , washed with Et_2O , dissolved in MeCN, and precipitated with Et_2O to obtain dyes **Va, b, and VI**.

1-Methyl-8-[(*p*-dimethylaminophenyl)ethenyl]-2-(*p*-X-tetrafluorophenyl)-4-phenyl-5,6,7,8-tetrahydro-1-quinolinium perchlorates (VIIIa, b). A mixture of 0.5 mmol of dye **Va, b**, 2 ml (5 mmol) of 10% solution of MeNH_2 in ethanol, and 2 ml of DMSO was stirred for 1 h at 100°C. The reaction mixture was cooled, poured into a saturated water solution of sodium perchlorate, the separated precipitate was filtered off, washed with water, dried in air, and washed with ethyl ether. The products were isolated by chromatography on a column packed with Al_2O_3 , eluent CH_2Cl_2 -MeCN, 4:1.

Reaction of styryl (VI) with methylamine. A product obtained by the above procedure from dye **VI** and MeNH_2 was washed with hexane and subjected to column chromatography on Al_2O_3 , eluent CH_2Cl_2 -MeCN, 4:1. From the first fraction compound **X** was isolated in 80% yield, in the second fraction the presence of dye **IX** was detected by ^{19}F NMR spectroscopy.

4-Methylamino-6-(*p*-dimethylaminophenyl)-1-pentafluorobenzoyl-2-phenyl-1,3-cyclohexadiene (X). mp 213–214°C. IR spectrum, ν , cm^{-1} : 1499 (C_6F_5), 1612 ($\text{C}=\text{O}$), 2816–3010 ($\text{C}_{\text{Alk}}-\text{H}$, $\text{C}_{\text{Ar}}-\text{H}$), 3445 (NH). ^1H NMR spectrum, δ , ppm: 2.41 d (1H, H^5 , J 16 Hz), 2.67 d (3H, NHMe , J 5.5 Hz), 2.90 s (6H, NMe_2), 3.10 br.d.d (1H, H^5 , J_1 16, J_2 7 Hz), 4.48 br.d (1H, H^6 , J 7 Hz), 4.78 s (1H, H^3), 5.27 br.q (1H, NH), 6.68 br.d (2H, $\text{H}^{3'}$, $\text{H}^{5'}$, J 7 Hz), 7.12 m (3H, H^3 , H^4 , H^5), 7.20 m (2H, H^2 , H^6), 7.26 m (2H, $\text{H}^{2'}$, $\text{H}^{6'}$). ^{19}F NMR spectrum, δ , ppm (intensity ratio): -1.55, 5.53, 20.97 (2:1:2). ^{13}C NMR spectrum, δ , ppm: 29.79 (NHCH_3), 37.00 (C^3), 37.25 (C^6), 40.60 (NMe_2), 96.49 (C^3), 112.79 ($\text{C}^{3'}$, $\text{C}^{5'}$), 118.87 ($\text{C}^{1''}$), 122.79 (C^1), 127.38 (C^3 , C^5), 127.80 (C^2 , C^6 , $\text{C}^{2'}$, $\text{C}^{6'}$), 128.05 (C^4), 130.69 ($\text{C}^{1'}$), 136.50 δ ($\text{C}^{3''}$, $\text{C}^{5''}$), 139.90 ($\text{C}^{4''}$), 141.98 (C^7), 142.10 d ($\text{C}^{2''}$, $\text{C}^{6''}$), 149.22 ($\text{C}^{4'}$), 156.84 (C^4), 160.00 (C^2), 179.77 ($\text{C}=\text{O}$). Found, %: C 67.90; H 4.89; F 18.97; N 5.52. M^+ 498.17257. $\text{C}_{28}\text{H}_{23}\text{F}_5\text{N}_2\text{O}$. Calculated, %: C 67.46; H 4.65; F 19.01; N 5.62. M 498.17304.

2-[(*p*-Dimethylaminophenyl)ethenyl]-4-phenyl-6-pentafluorophenylpyridinium perchlorate (IX). A

Table 2. ^1H and ^{19}F NMR spectra of dyes **Va, b, VI, VIIIa, b, IX, XIIa, b, XIIIa, b**

Compd. no.	^1H NMR spectra, δ , ppm	^{19}F NMR spectra, δ , ppm (intensity ratio)
Va	1.90 m (2H, CH_2), 2.95 br.t (2H, CH_2), 3.06 br.t (2H, CH_2), 3.18 s (6H, NMe_2), 6.76 d (2H, $\text{C}_6\text{H}_4\text{NMe}_2$), 7.46 s (1H, H_{Ht}), 7.54 s (5H, Ph), 7.66 d (2H, $\text{C}_6\text{H}_4\text{NMe}_2$), 8.14 s (1H, =CH)	3.00, 15.92, 23.36 (2:1:2)
Vb^a	1.93 m (2H, CH_2), 2.89 br.t (2H, CH_2), 3.04 br.t (2H, CH_2), 3.14 s (6H, NMe_2), 4.24 t (3H, OMe), 6.86 d (2H, $\text{C}_6\text{H}_4\text{NMe}_2$), 7.58 m (6H, Ph, H_{Ht}), 7.71 d (2H, $\text{C}_6\text{H}_4\text{NMe}_2$), 8.16 s (1H, =CH)	6.30, 22.04 (1:1)
VI^b	3.18 s (6H, NMe_2), 6.93 d (2H, $\text{C}_6\text{H}_4\text{NMe}_2$), 7.27 d (1H, CH^α , 15 Hz), 7.73 (m, 3H, Ph), 7.82 d (2H, $\text{C}_6\text{H}_4\text{NMe}_2$), 8.15 (2H, Ph), 8.26 s (1H, H_{Ht}), 8.37 br.d (1H, CH°), 8.45 br.s (1H, H_{Ht})	7.74, 20.89, 29.80 (2:1:2)
VIIIa	1.93 m (2H, CH_2), 2.66 m (2H, CH_2), 3.03 m (8H, CH_2 , NMe_2), 3.19 m (3H, NHMe), 4.24 s (3H, $\text{N}_{\text{Ht}}\text{Me}$), 4.75 br.s (1H, NHMe), 6.71 d (2H, $\text{C}_6\text{H}_4\text{NMe}_2$), 6.82 s (1H, =CH), 7.35–7.55 m (8H, H_{Ht} , arom)	1.70, 19.79 (1:1)
VIIIb	1.93 m (2H, CH_2), 2.67 m (2H, CH_2), 3.03 m (8H, CH_2 , NMe_2), 4.19 t (3H, OMe), 4.26 m (3H, $\text{N}_{\text{Ht}}\text{Me}$), 6.70 d (2H, $\text{C}_6\text{H}_4\text{NMe}_2$), 6.84 s (1H, =CH), 7.40–7.60 m (8H, H_{Ht} , arom)	6.89, 22.27 (1:1)
IX^a	3.06 s (6H, NMe_2), 4.01 s (3H, $\text{N}_{\text{Ht}}\text{Me}$), 6.82 d (2H, $\text{C}_6\text{H}_4\text{NMe}_2$), 7.70 d (2H, $\text{C}_6\text{H}_4\text{NMe}_2$), 7.16 d (1H, =CH), 7.96 m (1H, =CH), 7.63 m (3H, Ph), 7.97 m (3H, Ph, H_{Ht}), 8.57 d (1H, H_{Ht})	3.28, 14.48, 25.20 (2:1:2)
XIIa	1.72 m (2H, CH_2), 1.82 m (2H, CH_2), 2.53 m (2H, CH_2), 2.70 m (2H, CH_2), 2.87 m (2H, CH_2), 3.06 m (2H, CH_2), 3.13 m (3H, NHMe), 3.20 m (3H, NHMe), 4.14 s (3H, $\text{N}_{\text{Ht}}\text{Me}$), 4.46 br.s (1H, NH), 4.96 br.s (1H, NH), 6.04 s (1H, =CH), 7.10–7.50 m (12H, Ph, H_{Ht})	0.46, 1.65, 17.57, 18.87 (1:1:1:1)
XIIb	1.75 m (2H, CH_2), 1.87 m (2H, CH_2), 2.56 m (2H, CH_2), 2.72 m (2H, CH_2), 2.87 m (2H, CH_2), 3.07 m (2H, CH_2), 4.11 s (3H, $\text{N}_{\text{Ht}}\text{Me}$), 4.23 t (6H, OMe), 6.12 s (1H, =CH), 7.09–7.50 m (12H, Ph, H_{Ht})	4.76, 6.81, 19.92, 21.70 (1:1:1:1)
XIIIa	1.74 m (4H, CH_2), 2.65 m (4H, CH_2), 2.75 m (4H, CH_2), 3.14 br.s (6H, NHMe), 3.60 s (6H, $\text{N}_{\text{Ht}}\text{Me}$), 4.59 br.s (1H, NH), 6.41 s (1H, =CH), 6.69 s (2H, H_{Ht}), 7.20–7.50 m (10H, Ph)	1.54, 17.93(1:1)
XIIIb	1.75 m (4H, CH_2), 2.67 (4H, CH_2), 2.80 m (4H, CH_2), 3.62 s (6H, $\text{N}_{\text{Ht}}\text{Me}$), 4.13 s (6H, OMe), 6.39 s (1H, =CH), 6.72 s (2H, H_{Ht}), 7.30–7.50 m (10H, Ph)	6.46, 20.37(1:1)

^a C CD_3CN . ^b C $(\text{CD}_3)_2\text{SO}$.

mixture of 0.45 g (1 mmol) of pyridinium salt **III** and 0.45 g (3 mmol) of aldehyde **VII** in 2 ml of a mixture of Ac_2O and AcOH , 1:1, was heated on a bath of 120°C for 3 h. On cooling the reaction mixture was poured into Et_2O , thoroughly ground, the separated precipitate was filtered off, washed with Et_2O , and subjected to chromatography on Al_2O_3 , eluent CH_2Cl_2 – MeCN , 10:1.

Reaction of pyrilocyanines (XIa, b) with methylamine. (a) A mixture of 0.5 mmol of initial dye **XIa, b** and 2 ml (5 mmol) of 10% solution of MeNH_2 in EtOH was stirred for 3 h at room temperature, then poured into a saturated water solution of sodium perchlorate, the separated precipitate was filtered off and washed with water. After treating the reaction product with ether and chromatography on Al_2O_3 (eluent CH_2Cl_2 – MeCN , 4:1) we

obtained 1-methyl-2-(*p*-X-tetrafluoro-phenyl)-4-phenyl-5,6,7,8-tetrahydro-8-[(2-*p*-X-tetrafluorophenyl-4-phenyl-6,7-dihydro-5*H*-1-benzopyranyl-8-yl)methylene]-1-quinolinium perchlorate (**XIIa, b**).

(b) A mixture of 0.5 mmol of pyrilocyanine **XIa, b**, 2 ml (10 mmol) of 20% solution of MeNH_2 in EtOH , and 2 ml of DMSO was stirred for 3 h at room temperature, then poured into a saturated water solution of sodium perchlorate, the separated precipitate was filtered off and washed with water.

The product obtained from dye **XIa** was dissolved in a little of ethanol (~1 ml) and reprecipitated with ethyl ether to furnish 0.03 g (7%) of 1-methyl-2-(*p*-methylaminotetrafluorophenyl)-8-[(1-methyl-2-*p*-methylaminotetrafluorophenyl-4-phenyl-5,6,7,8-

tetrahydroquinolino-8-yl)-methylene]-4-phenyl-5,6,7,8-tetrahydro-1-quinolinium perchlorate (**XIIIa**). The residue insoluble in EtOH was subjected to column chromatography on Al_2O_3 (eluent CH_2Cl_2) to isolate 0.16 g (50%) of compound **XIVa**.

1-Methyl-2-(*p*-methoxytetrafluorophenyl)-8-[(1-methyl-2-*p*-methoxytetrafluorophenyl-4-phenyl-5,6,7,8-tetrahydroquinolin-8-yl)methylene]-4-phenyl-5,6,7,8-tetrahydro-1-quinolinium perchlorate (XIIIb**)** was isolated by washing with ethyl ether the reaction product obtained from dye **XIb**, yield 0.11 g (24%). Evaporation of the filtrate and subsequent column chromatography on Al_2O_3 afforded 0.21 g (66%) of pyridone **XIVb**.

1-Methyl-8-[(2-*p*-methylaminotetrafluorophenyl-4-phenyl-6,7-dihydro-5*H*-1-benzopyran-8-yl)-methylene]-4-phenyl-5,6,7,8-tetrahydrobenzo-2-pyridone (XIVa**)**, mp 143–146°C. IR spectrum (CHCl_3), ν , cm^{-1} : 1499 (C_6F_5), 1642 (C=O), 3443 (NH). ^1H NMR spectrum, δ , ppm: 1.55, 1.62, 1.85, 2.10, 2.18, 2.45, 2.65 all m (12H, CH_2), 3.10* and 3.13 both br.s (3H each, NHMe), 3.53 and 3.68* both s (3H each, $\text{N}_{\text{Ht}}\text{Me}$), 4.05 br.s (2H, NH), 5.81* and 5.88 both s (1H each, H^3), 6.39* and 6.45 both s (1H each, H^3), 6.57 and 6.76 both s (1H each, H^α), 7.18–7.45 m (10H, Ph). Asterisks mark the signals of the minor isomer, intensity ratio 3:4. ^{19}F NMR spectrum, δ , ppm (intensity ratio): 0.10, 0.54, 18.50, 18.93 (3:4:3:4). Found, %: F 12.39; N 4.27. M^+ 636.23803. $\text{C}_{39}\text{H}_{32}\text{F}_4\text{N}_2\text{O}_2$. Calculated, %: F 11.94; N 4.40. M 636.23997.

1-Methyl-8-[(2-*p*-methoxytetrafluorophenyl-4-phenyl-6,7-dihydro-5*H*-1-benzopyran-8-yl)-methylene]-4-phenyl-5,6,7,8-tetrahydrobenzo-2-pyridone (XIVb**)**, mp 111–113°C. IR spectrum (CHCl_3), ν , cm^{-1} : 1489 (C_6F_5), 1648 (C=O). ^1H NMR spectrum, δ , ppm: 1.55–1.95, 2.23, 2.50–2.62 all m (12H, CH_2), 3.48 and 3.60 both s (3H each, $\text{N}_{\text{Ht}}\text{Me}$), 4.08* and 4.11 both t (3H each, OMe), 5.87* and 5.95 both s (1H each, H^3), 6.24* and 6.32 both s (1H each, H^3), 6.54* and 6.71 both s (1H each, =CH), 7.20–7.40 m (10H, Ph). Asterisks mark the signals of the minor isomer, intensity ratio 3:4. ^{19}F NMR spectrum, δ , ppm (intensity ratio): 4.25, 4.53, 20.40, 20.60 (4:3:3:4). Found, %: C 73.87; H 4.55; F 12.39; N 2.10. M^+ 637.22250. $\text{C}_{39}\text{H}_{31}\text{F}_4\text{NO}_3$. Calculated: C 73.46; H 4.90; F 11.92; N 2.20. M 637.22399.

Reaction of dyes **XIIa**, **b** with methylamine.

A mixture of 0.5 mmol of pyrilo-pyridocyanine **XIIa**, **b**, 2 ml (10 mmol) of 20% MeNH_2 solution in EtOH, and 2 ml of DMSO was stirred for 3 h at room tem-

perature, then was poured into a saturated water solution of sodium perchlorate, the separated precipitate was filtered off, washed with water and Et_2O .

1-Methyl-8-(*p*-dimethylaminophenyl)-ethenyl-2,4-diphenyl-5,6,7,8-tetrahydro-1-quinolinium perchlorate (XVd**)** was prepared from an appropriate pyrilocyanine and methylamine in the same way as dyes of **VIII** type. After subjecting the product to column chromatography on Al_2O_3 the dye was recrystallized from a mixture $\text{EtOH-H}_2\text{O}$, 2:1.

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