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PYRILOCYANINES.
37*. PYRILO-2-CYANINES WITH PERFLUOROPHENYL SUBSTITUENTS

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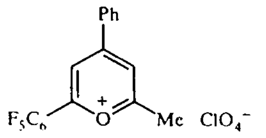
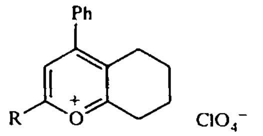
Symmetrical and nonsymmetrical pyrilo-2-cyanines have been synthesized containing the 6-perfluorophenyl-4-phenylpyrilium residue. As an example of these compounds we have analyzed the effect of changing phenyl groups for perfluorophenyl in terms of the long wavelength electronic absorption spectra for the above types of dyes. It was found that this change leads to a decrease in the effective length and the electron donor ability of hetero residues containing these groups. The former effect gives rise to a hypsochromic shift of the absorption band and the second to a broadening of these bands associated with increased vibrational interactions in the molecules and their solvates.

In [2], as an illustration of symmetrical 4,4',6,6'-tetraphenyl substituted pyrilo-2-carbocyanines, it was shown that introduction of a substituent (R) of different electron type in the para position to the phenyl groups can directly affect the position, intensity, and form of the absorption band. It was found that both typical electron donors (R = OCH_3) and electron acceptor (R = NO_2) substituents act upon the color in one sense, i.e., to deepen it [2]. One of the basic reasons for this is the potential lengthening of the chromophore in the direction of the introduced substituent R. Hence a judgement of the influence of the electronic effect of the latter on the color for such a substitution is difficult.

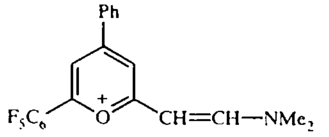


I

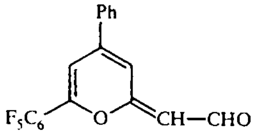


IIa, b

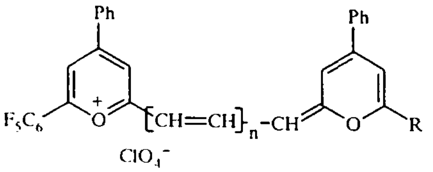
II a R = C_6F_5; b R = C_6F_4OMe



III ClO_4^-



IV



Va, b ; VIa, b

Va, b n = 1; VIa, b n = 2; V, VI a R = C_6F_5, b R = Ph

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*For Communication 36 see [1].

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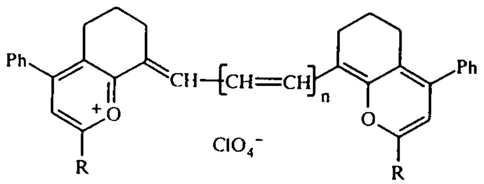
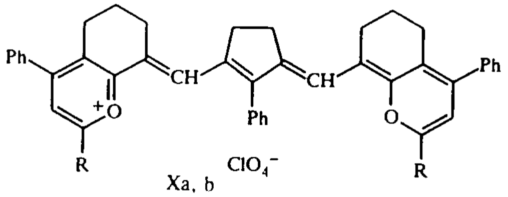


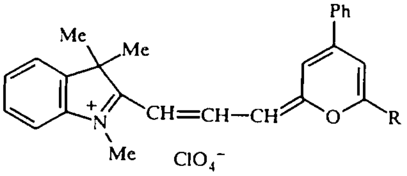
VIIa-c, VIIIa, b, IXa, b

VIIa-c n = 0; VIIIa,b n = 1; VII-IX a R = C_6F_5,
b R = Ph, c R = C_6F_4-OMe-*p*



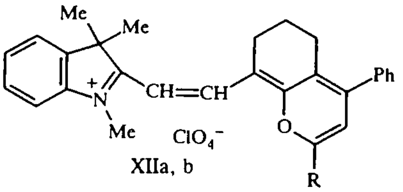
Xa, b

X a R = C_6F_5; b R = Ph



XIa, b

XI a R = C_6F_5; b R = Ph



XIIa, b

XII a R = C_6F_5; b R = Ph

In this work we have synthesized pyrilo-2-cyanines containing at positions 6 and 6′ perfluorophenyl groups not able significantly to lengthen the chromophore with relation to the phenyl analogs and studied the electronic absorption spectra of these compounds relative to the former. To prepare the indicated dyes we used the salts I-III [3] and 2-formylmethylene-2H-pyran (IV) which is the product of basic hydrolysis of salt III [4, 5]. Carrying out the reaction in acetonitrile solution gave a significant increase in the yield of aldehyde IV (80% compared with 21% quoted in [5]).

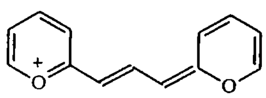
The target dyes Va-XIIa and VIIc were prepared from I-IV. Carbocyanines Va, VIIa, c were prepared by condensation of the corresponding pyrilium salts with ethyl orthoformate, carried out in a mixture of acetic acid and acetic anhydride in the presence of anhydrous sodium acetate. Dye Va was prepared in this way in low yield (12%). It was found that a much higher yield of this compound (50%) could be achieved by carrying out by reaction of the pyrilium salt I with aldehyde IV. The dicarbocyanines VIa and VIIIa were prepared by condensation of the corresponding pyrilium salts I and IIa with phenyl(3-phenylaminoprop-2-enylidene)ammonium chloride using the conditions described above for synthesizing the carbocyanines.

Tricarbocyanines IXa and Xa were synthesized in the same conditions as for salt IIa respectively with phenyl(5-phenylaminopenta-2,4-dienylidene)ammonium chloride and its analog with a dimethylene bridge in the chain.

The unsymmetrical (pyrilo)(indo)trimethinecyanines XIa and XIIa were prepared from the corresponding I, IIa, and 1,3,3-trimethyl-2-formylmethylene-3H-indolium salts in acetic anhydride.

For solutions of the perfluorophenyl substituted symmetrical (Va-Xa) and unsymmetrical (XIa, XIIa) dyes in methylene chloride and acetonitrile, Tables 1 and 2 show λ_{max} and log ε together with mid band positions M^{-1} determined by the method of moments, the oscillator strength f, the width σ, the asymmetry coefficient γ_1, the excess γ_2, the fine structure F, and the radiative life time τ_r of the first excited state [6]. For comparison, there are also included analogous parameters for the corresponding, known phenyl substituted dyes (Vb-XIIb).

From the values of λ_{max} and M^{-1} in Table 1 it is apparent that the absorption bands in both solvents for the symmetrical dyes Va-Xa with substituents R = C_6F_5 are hypsochromically shifted relative to the bands of the corresponding compounds Vb-Xb having R = C_6H_5. Such a difference can be related to electronic and steric effects for the indicated substituents. From quantum chemical calculations for cation XIII, carried out similarly to [2], it follows that the electron density at positions 6 and 6′ is increased with excitation. According to MO perturbation theory [7], introduction of electron acceptor substituents which include perfluorophenyl groups, should lead to a bathochromic shift. Hence, in our case, a reverse pattern is observed and it can be concluded that the dominant effect on the color of the fluro containing dyes is a steric factor. In fact,



XIII

as a result of steric hindrances between the ortho fluoro atoms and the pyrilium ring the C_6F_5 ring is displaced significantly from the chromophore plane whereas the torsional angle for the C_6F_5 group does not exceed 10° from this plane [8]. Hence the hypsochromic shift on crossing from Vb-Xb to Va-Xa is mainly due to the decreased degree of conjugation for the perfluorophenyl groups compared with the phenyl in positions 6 and 6′. These circumstances are in agreement with a lower value of the extinction and oscillator strengths for cyanines Va-Xa compared with Vb-Xb.

Change from the carbocyanine VIIa, containing the C_6F_5 group, to its analog VIIc with the $C_6F_4OCH_3$-p is accompanied by a deepening of the color by 8 and 9 nm in methylene chloride and acetonitrile respectively thanks to the increasing effective length of the terminal pyrilium rings due to a change of the fluorine atom for an electron donor methoxy group. The latter effect also explains the shift to higher field (by 0.34 ppm) for the pyrilium 5-H proton signal in the PMR spectrum of VIIc relative to the analogous proton in VIIa (see Table 1 and Experimental section).

The radiative life time is calculated from the formula:

$$\tau_p = \frac{1{,}511 \cdot 10^9}{f \bar{\nu}^2}$$

where $\bar{\nu} = 10^7/M^{-1}$ which is the mean normalized distribution of the photons (center of gravity of the band) in cm^{-1}. This value is of interest for the theory of nonradiative processes, particularly on changing the C–H bond (having a high frequency valence vibration), for the low frequency C–F bonds. In fact, overtones of the first show a marked effect on the deactivation of the electron excited states of the dye, absorbing in the near IR region of the spectrum (as a result of partial overlap with the bands of their long wavelength electronic transitions [6]). Lowering of the frequency of such vibrations upon change of hydrogen atoms for fluorine decreases the degree of overlap mentioned which can affect the nonradiative process. From Table 1 it is seen that the values of τ_r for the perfluorophenyl substituted pyrilocyanines Va-Xa are greater than for the phenyl substituted Vb-Xb. Basically this difference rests on two concurrent factors, the oscillator strengths and mean frequency. Decrease of the first on going from Vb-Xb to Va-Xa must lead to an increase in τ_r in this series and an increase in $\bar{\nu}$ for this transition, on the other hand, to a lowering of the radiative time. From the experimental data it follows that increase in τ_r on going from phenyl groups in pyrilocyanines Vb-Xb to perfluorophenyl is principally linked to a lowering of f for such a change.

The perfluorophenyl substituted dyes Va-Xa, like their phenyl counterparts Vb-Xb, have broad bands with strongly pronounced vibrational structure. As a consequence, there exists with the first, as well as the latter, a significant contribution of excitation of the $C_{(3)}-C_{(4)}$ bond of the pyran residues to the formation of the band profile as a part of which there occurs a third contribution for the vibrational interaction of the whole cation [9]. However, the absorption bands of the pyrilocyanines Va-Xa are broader than the similar bands for the corresponding dyes Vb-Xb ($R = C_6H_5$) (Table 1). What has been said occurs both with the weakly solvating methylene chloride and with the strongly solvating acetonitrile. Broadening of the bands on going from dyes Vb-Xb to Va-Xa is accompanied in the first solvent by a decrease in the asymmetry coefficient, excess, and fine structure and in the second by a change in the value of σ in line with the coefficients γ_1, γ_2, and F (Table 1). Such a change of the characteristic profile of the bands, as follows from [6], shows that the different profile for Va-Xa and Vb-Xb is determined in methylene chloride principally by vibrational interactions and in acetonitrile by intermolecular interactions with the solvent. The greater solvation of the fluoro containing pyrilocyanines is also confirmed by the larger values of the band broadening $\Delta\sigma$ when compared with the same values for their phenyl substituted analogs upon change of methylene chloride for acetonitrile. Moreover, the difference in the indicated values for dyes Va-IXa and Vb-IXb increases with chain length. Hence in the series of pyrilocyanines Va-IXa, $\Delta\sigma$ are respectively 148, 298, 137, 229, and 815 and in the series Vb-IXb 103, 191, 90, 170, and 734 cm^{-1}. Similar effects with change of solvent are observed for values of $\Delta\bar{\nu}$. For Va-IXa these are 360, 537, 245, 416, and 1005 and for Vb-IXb 337, 423, 227, 352, and 921 cm^{-1}.

It should also be mentioned that the growth of n leading to a more powerful solvation of the fluoro dyes Va-IXa when compared with their analogs Vb-IXb having unsubstituted phenyl substituents also occurs in methylene chloride. This is shown, on the one hand, by the smaller values of absorption band narrowing upon lengthening of the polymethine chain for pyrilocyanines with saturated cyclic groups VIIa-IXa compared with the same values for analogs VIIb-IXb. On the other hand,

TABLE 1. Parameters for the Longwavelength Absorption Bands for Solutions of Dyes Va, b-Xa, b in Methylene Chloride and Acetonitrile

Compound	Solvent*	λ_{max}, nm	log ε	M^{-1}, nm	f	σ, cm^{-1}	γ_1	γ_2	F	t_r
Va	1	710, 780	4,79; 4,89	720,1	0,66	1217	1,05	1,6	0,063	11,9
	2	702, 769	4,75; 4,79	701,9	0,70	1365	1,19	2,6	0,059	10,6
Vb	1	730, 800	4,77; 4,93	739,6	0,78	1176	1,17	2,2	0,064	10,6
	2	725, 790	4,76; 4,80	721,6	0,77	1279	1,09	1,9	0,057	10,2
VIa	1	800, 890	4,90; 5,05	814,2	1,05	1251	1,20	1,7	0,080	9,56
	2	789, 870	4,80; 4,83	780,1	0,90	1549	1,55	4,0	0,098	10,2
VIb	1	820, 910	4,91; 5,08	839,5	1,12	1137	1,32	2,9	0,083	9,51
	2	808, 895	4,88; 4,93	810,7	1,05	1328	1,26	2,7	0,067	9,46
VIIa	1	742, 820	4,65; 4,79	751,2	0,44	1201	1,23	2,5	0,071	19,4
	2	736, 804	4,52; 4,58	737,6	0,46	1338	1,43	3,6	0,079	17,9
VIIb	1	760, 835	4,59; 4,79	781,9	0,51	1146	1,26	2,7	0,074	18,1
	2	830	4,72	768,3	0,53	1236	1,29	2,8	0,068	16,8
VIIIa	1	820, 910	4,85; 5,06	838,1	0,70	1138	1,36	3,0	0,088	15,2
	2	808, 890	4,68; 4,76	809,9	0,65	1367	1,50	3,8	0,089	15,3
VIIIb	1	845, 940	4,88; 5,14	874,4	0,96	1071	1,44	3,4	0,092	12,0
	2	930	4,96	848,3	0,87	1241	1,32	3,0	0,075	12,5
IXa	1	910, 1015	4,98; 5,21	942,6	0,95	1108	1,38	3,1	0,089	14,1
	2	893, 993	4,77; 4,79	861,0	0,86	1923	1,72	4,8	0,114	13,0
IXb	1	934, 1050	4,92; 5,20	971,9	1,07	1022	1,47	3,4	0,099	13,3
	2	1033	4,91	892,1	1,10	1756	1,70	4,7	0,112	10,9
Xa	1	965, 1085	4,89; 5,08	987,5	0,82	1220	1,15	1,8	0,059	18,0
Xb	1	1005, 1136	4,9; 5,10	1044,5	0,96	1080	1,20	2,1	0,063	17,2

*Methylene chloride (1), acetonitrile (2).

TABLE 2. Parameters for the Longwavelength Absorption Bands of Dyes XIa, b and XIIa, b in Methylene Chloride and Acetonitrile

Compound	Solvent*	λ_{max}, nm	log ε	M^{-1}, nm	D_M, nm	f	σ, cm^{-1}	γ_1	γ_2	F	τ_r, nsec
XIa	1	610, 655	4,58; 4,60	611,2	11,9	0,79	1951	0,86	1,4	0,030	7,16
	2	610, 640	4,60; 4,59	601,8	9,1	0,82	2162	0,99	2,2	0,047	6,71
XIb	1	654, 682	4,71; 4,63	641,1	-8,3	0,76	1450	0,89	1,5	0,031	8,17
	2	650	4,72	630,0	-9,3	0,83	1616	0,87	1,7	0,030	7,26
XIIa	1	612, 652	4,62; 4,68	624,4	14,2	0,79	1704	0,92	2,0	0,035	7,47
	2	605, 640	4,60; 4,63	609,1	19,6	0,76	1826	1,02	2,4	0,046	7,37
XIIb	1	660, 706	4,76; 4,68	651,6	2,4	0,78	1380	1,01	2,0	0,039	8,22
	2	657	4,71	640,9	3,2	0,74	1470	0,95	1,9	0,033	8,47

*Methylene chloride (1), acetonitrile (2).

this causes broadening of the bands in the series of fluoro dyes Va, VIIa with an open chain, in contrast to their analogs Vb, VIb for which growth in *n* leads to band narrowing in methylene chloride (Table 1). The latter, in the absence of powerful solvating effects, can occur with lengthening of the polymethine chain since growth of *n* for the symmetrical dyes is accompanied by progressive weakening of vibrational interactions [6].

The absorption band shape of the unsymmetrical dyes XIa, b and XIIa, b is quite complex (see Fig. 1) if, for values of λ_{max}, one is to make objective conclusions about the coloring and deviation values characterizing the electron donor ability (basicity) of the hetero residues (even though these compounds belong to the same structural type). Its complexity is due on the one hand to the fact that the change of electron asymmetry for the band maximum can be attributed to various vibrational transitions. On the other hand the band splitting of a pure electron transition involves not only a full symmetry valence vibration of the carbon–carbon bonds of the principal axis of the chromophore but also the $C_{(3)}-C_{(4)}$ bond. For the same reasons it is

TABLE 3. Parameters for Synthesized Compounds

Compound	Empirical formula	$\frac{\text{Found, \%}}{\text{Calculated, \%}}$				mp,* °C	Yield, %
		C	H	Cl	F		
III	$C_{21}H_{15}ClNF_5O_5$	$\frac{51,1}{51,3}$	$\frac{2,9}{3,0}$	$\frac{7,3}{7,2}$	$\frac{19,2}{19,3}$	209...210	76
IV	$C_{19}H_9F_5O_2$	$\frac{62,8}{62,6}$	$\frac{2,6}{2,5}$	—	$\frac{25,8}{26,1}$	112...113	80
Va	$C_{37}H_{17}ClF_{10}O_6$	—	—	$\frac{4,6}{4,5}$	$\frac{24,3}{24,3}$	291...292	50
VIa	$C_{39}H_{19}ClF_{10}O_6$	$\frac{57,6}{57,9}$	$\frac{2,3}{2,3}$	—	$\frac{23,4}{23,5}$	225...226	14
VIIa	$C_{43}H_{25}ClF_{10}O_6$	$\frac{59,9}{59,8}$	$\frac{3,0}{2,9}$	$\frac{3,9}{4,1}$	$\frac{21,5}{22,0}$	170...171	73
VIIc	$C_{45}H_{31}ClF_8O_8$	$\frac{61,2}{60,9}$	$\frac{3,6}{3,5}$	$\frac{4,5}{4,0}$	$\frac{17,0}{17,1}$	287...289	73
VIIIa	$C_{45}H_{27}ClF_{10}O_6$	$\frac{60,3}{60,8}$	$\frac{3,0}{3,0}$	$\frac{3,7}{3,9}$	$\frac{21,3}{21,4}$	197...198	67
IXa	$C_{47}H_{29}ClF_{10}O_6$	$\frac{62,2}{61,7}$	$\frac{3,5}{3,2}$	—	$\frac{20,2}{20,7}$	210...211	45
Xa	$C_{55}H_{35}ClF_{10}O_6$	$\frac{65,1}{64,9}$	$\frac{3,4}{3,5}$	$\frac{3,4}{3,5}$	$\frac{18,2}{18,7}$	163...164	46
XIa	$C_{31}H_{23}ClNF_5O_5$	—	—	$\frac{5,8}{5,7}$	$\frac{15,3}{15,3}$	147...148	18
XIIa	$C_{34}H_{27}ClNF_5O_5$	—	—	$\frac{4,9}{5,3}$	$\frac{14,4}{14,4}$	240...241	49

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*Compounds III, VIIa, VIIIa, VIIc, Xa, and XIIa were crystallized from acetic acid, IV from aqueous alcohol, Va, VIa, IXa from acetonitrile, and XIa from aqueous acetic acid.

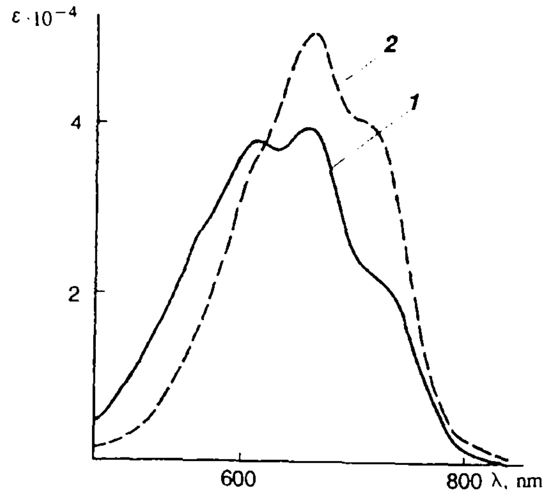

Fig. 1. Electronic absorption spectra of the unsymmetrical dyes XIa (1) and XIb (2) in methylene chloride (C ~ 2 × 10^{-5}).

difficult to correlate the electron donor ability with relation to the intensity of the principal and secondary peak maxima. The values of M^{-1} are averaged for all vibrational sublevels and hence give a direct value for the position of the bands of the other form. From comparison of these values it is apparent that the perfluorophenyl substituted dyes XIa, XIIa absorb light at a shorter wavelength region of the spectrum than the phenyl analogs XIb, XIIb.

It was difficult to make unambiguous conclusions about the relative electron donor abilities of the terminal hetero residues from the values of the deviation D_M calculated from M^{-1} and this is evidently connected with the large difference in the absorption regions of the parent dyes (>200 nm in M^{-1}) (see [6, 10, 11]). However, this could be achieved through analysis of the change in band width of the unsymmetrical dyes. Starting from the fact that the value of σ for the fluoro compounds XIa, XIIa is significantly larger than for analogs XIb, XIIb in dichloromethane and acetonitrile it follows that the former is more electron asymmetric that the latter. Since the pyrilium residue has a lower electron donor ability than indolium [2] it can be deduced that change of the C_6H_5 groups at position 6,6' of the pyrilocyanines to the electron acceptor C_6F_5 groups leads to a lowering of the electron donor ability of the pyran residues.

Increase in electron asymmetry on going from XIb, XIIb to XIa, XIIa causes increased depth of color. The additional contribution of this increase leads to a smaller effective length for the fluorophenyl substituted pyrilium residues (shorter wavelength absorption for the fluoro symmetrical dyes) when compared with those with phenyl substituents (Table 1).

Lowering of the electron donor ability on exchanging the C_6H_5 groups in the symmetrical pyrilocyanines Vb-Xb for C_6F_5 groups in Va-Xa increases the bond order alternation in the chain from the center to the rings (see [2]). This leads to strengthening of the vibrational interactions which is mainly seen as a broadening of the absorption bands and decreasing intensity (ε and f), asymmetry, slope and structuring on crossing from Vb-Xb to Va-Xa in the weakly nucleophilic methylene chloride. In addition, increase in the deviation of the electron donor ability of the hetero residues from its mean value (close to those with an indole ring [2]) increases the nonuniformity of charge distribution and hence strengthening the nucleophilic solvation on going from phenyl to perfluorophenyl substituted pyrilocyanines Vb-Xb to Va-Xa. Introduction of electron donor, saturated, bridging groups increases the electron donor ability of the pyran residues as indicated by the lower value of σ for the unsymmetrical pyrilocyanines XIIa, b compared to XIa, b. Hence for the symmetrical dyes VIIa-IXa, VIIb-IXb, having saturated cyclic groups and increasing the uniformity in charge distribution [12], solvating effects are markedly weaker than for compounds with open chains Va, VIa and Vb, VIb (see, e.g. the values for $\Delta\sigma$ in methylene chloride and acetonitrile).

The characteristic change in values of σ, γ_1, γ_2, and F on going from unsymmetrical dyes XIa, XIIa ($R = C_6F_5$) to analogs XIb, XIIb ($R = C_6H_5$) in methylene chloride and acetonitrile are similar to those in the corresponding series of symmetrical compounds Va, VIIa and Vb, VIIb.

By contrast with the symmetrical compounds Vb, VIIb, the exchange of phenyl for perfluorophenyl groups in the symmetrical pyrilocyanines XIb, XIIb causes a decrease in the radiative life times (Tables 1 and 2). This change is a result of the fact that the oscillator strength in the first case changes less than in the latter. As a result of this specific role in changing τ_r for the unsymmetrical dyes, an increase in $\bar{\nu}$ is involved as a consequence of the hypsochromic shifts of M^{-1} on crossing from compounds XIb, XIIb to XIa, XIIa.

EXPERIMENTAL

Absorption spectra for compounds Va-XIIa, VIIc in methylene chloride (stabilized by 1% absolute ethanol) and in acetonitrile as well as dyes VIIb-IXb, XIb, XIIb in acetonitrile were measured on a Shimadzu UV-3100 spectrophotometer. Compound purity was monitored by TLC on Silufol UV-254 plates using acetonitrile eluent. NMR Spectra were taken on a Bruker WP-20054 spectrometer at 200 (^1H) or 188.2 (^{19}F) MHz. PMR Spectra were recorded using TMS as internal standard and ^{19}F NMR spectra using C_6F_6.

Spectral parameters for pyrilocyanines Vb-XIIb in methylene chloride were taken correspondingly from [13, 14, 12, 10, and 11] and dyes Va, VIb in acetonitrile from [9].

Mathematical treatment of the long wavelength absorptions using the method of moments was carried out using the modernized Moment program [15] for personal computers using Basic language.

2-[2-(Dimethylamino)vinyl]-6-(pentafluorophenyl)-4-phenylpyrilium Perchlorate (III). A mixture of salt I (0.436 g, 1 mmole) and DMF (1 g, 10 mmole) in acetic anhydride (10 ml) was held at 130-140°C for 30 min. After cooling, the reaction product was mixed with ether (200 ml), the precipitated product III filtered, and washed with ether. Yield 0.37 g.

2-Formylmethylene-6-pentafluorophenyl-4-phenyl-2H-pyran (IV). A mixture of salt III (0.37 g, 0.75 mmole) in acetonitrile (15 ml) and 5% aqueous sodium hydroxide solution (15 ml) was stirred for 1 h at room temperature and then poured in water and held for 2 days. The precipitated product IV was filtered, washed with water, and dried. Yield 0.22 g

2-[3-(6-pentaflorophenyl-4-phenylpyran-2-ylidene)prop-1-en-1-yl]6-pentafluorophenyl-4-phenylpyrilium Perchlorate (Va). A mixture of perchlorate I (0.2 mmole), anhydrous sodium acetate (0.2 mmole), and aldehyde IV (0.22 mole) in a mixture of glacial acetic acid and acetic anhydride (1:1, 1.5 ml) was refluxed for 3 min. The precipitated dye Va was filtered and washed with acetic acid and ether.

2-[5-(6-Pentafluorophenyl-4-phenylpyran-2-ylidene)penta-1,3-dien-1-yl]-6-pentafluorophenyl-4-phenylpyrilium perchlorate (VIa) was prepared from perchlorate I (0.5 mmole), anhydrous sodium acetate (0.5 mmole), and phenyl[3-phenylaminoprop-2-en-1-ylidene]ammonium chloride in the conditions used for synthesis of Va.

2-Pentafluorophenyl-4-phenyl-8-[(2-pentafluorophenyl-4-phenyl-6,7-dihydro-5H-1-benzopyran-8-yl)methylene]-5,6,7,8-tetrahydro-1-benzopyrilium perchlorate (VIIa) was prepared from salt IIa (0.25 mmole), anhydrous sodium acetate (0.25 mmole), and ethyl orthoformate (0.5 ml) similarly to dye Va. PMR Spectrum ($CDCl_3$): 1.83 (4H, m, 6-CH_2); 2.82 (4H, m, 5-CH_2); 2.96 (4H, m, 7-CH_2); 6.97 (2H, s, 3-CH); 7.48 (10H, m, Ph); 8.38 ppm (1H, s, meso-H). ^{19}F NMR Spectrum ($CDCl_3$): 1.52; 13.84; 22.59 ppm. Signal intensity ratio 2:1:2 respectively.

2-Pentafluorophenyl-4-phenyl-8-[3-(2-pentafluorophenyl-4-phenyl-6,7-dihydro-5H-1-benzopyran-8-yl)prop-2-en-1-ylidene]-5,6,7,8-tetrahydro-1-benzopyrilium perchlorate (VIIIa) was prepared from salt IIa similarly to dye VIa.

2-Pentafluorophenyl-4-phenyl-8-[5-(2-pentafluorophenyl-4-phenyl-6,7-dihydro-5H-1-benzopyran-8-yl)penta-2,4-dien-1-ylidene]-5,6,7,8-tetrahydro-1-benzopyrilium perchlorate (IXa) was prepared from salt IIa and phenyl[5-(phenylaminopenta-2,4-dienylidene)]ammonium chloride similarly to dye VIIIa.

2-(4-Methoxytetrafluorophenyl)-4-phenyl-8-{[2-(4-methoxytetrafluorophenyl)-4-phenyl-6,7-dihydro-5H-1-benzopyran-8-yl]methylene}-5,6,7,8-tetrahydro-1-benzopyrilium perchlorate (VIIc) was prepared similarly to dye VIIIa from salt IIb and ethyl orthoformate by refluxing for 30 min. The product was precipitated from nitromethane using ether. Electronic absorption spectrum, λ_{max}, nm (log ε), in CH_2Cl_2: 753 (4.67); 828 (4.79); in CH_3CN: 745 (4.62); 813 (4.67). PMR Spectrum (DMSO-D_6): 1.76 (4H, m, 6-CH_2); 2.95 (4H, m, 7-CH_2); 4.18 (6H, t, J = 1 Hz, OMe); 7.31 (5H); 7.58 (Ph); 8.40 ppm (meso-H). ^{19}F NMR Spectrum (DMSO-D_6): 4.48, 20.48 ppm. Signal intensity ratio 1:1.

8-[2,4-Dimethylene-5-(2-pentafluorophenyl-4-phenyl-6,7-dihydro-5H-1-benzopyran-8-yl)-3-phenylpenta-2,4-dien-1-ylidene]-2-pentafluorophenyl-4-phenyl-5,6,7,8-tetrahydro-1-benzopyrilium perchlorate (Xa) was prepared from salt IIa and phenyl[2,4-dimethylene-3-phenyl-5-(phenylaminopenta-2,4-dienylidene)]ammonium chloride similarly to dye IXa.

1,3,3-Trimethyl-2-[3-(4-phenyl-6-pentafluorophenylpyran-2-ylidene)prop-1-en-1-yl]-3H-indolium Perchlorate (XIa). A mixture of salt I (0.5 mmole), 1,3,3-trimethyl-2-formylmethylene-3H-indoline (0.55 mmole), and acetic anhydride (2 ml) was held at 130-135°C for 30 min. The dye was precipitated from acetonitrile with 20% perchloric acid.

1,3,3-Trimethyl-2-[2-(2-pentafluorophenyl-4-phenyl-6,7-dihydro-5H-1-benzopyran-8-yl)vinyl-3H-indolium perchlorate (XIIa) was prepared from salt IIa similarly to dye XIa. The product was precipitated using a saturated aqueous solution of sodium perchlorate.

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