SYNTHESIS OF DYES CONTAINING FLUORINE ATOMS IN THE POLYMETHINE CHAIN

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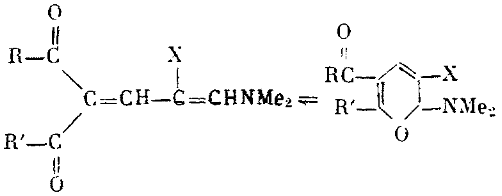
Based on α-fluoro-β-dimethylaminoacrolein aminal (I) [1], we synthesized new mero- and ketocyanins, pentacarbocyanins, and cation–anion cyanin dyes containing fluorine atoms in the polymethine chain.

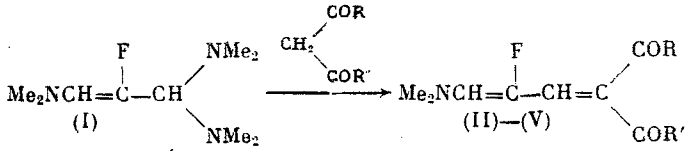
Many papers dealing with the effect of fluorine atoms and fluorine-containing substituents on dye properties have been published in the past few years [2]. The introduction of fluorine-containing substituents affords dyes that are stable to oxidation, light, and other physical effects. Some of these dyes have found practical use as spectral sensitizers in film photography. Fluorine atoms in polymethine chains have a much stronger effect on absorption spectra than those in heterocyclic nuclei.

Earlier [3-5] it was found that merocyanins (γ-substituted δ-dimethylaminodienones), as a result of δ-aminodienone ⇆ 2-amino-2H-pyran valence isomerization, exhibit solvato-, thermo-, and photochromic properties.



To study the effect of the fluorine atom in the γ-position of dienones on this isomerization, we condensed aminal (I) with several β-dicarbonyl compounds and obtained γ-fluoro-δ-dimethylaminodienones (II)-(V) (Table 1).

According to ^1H and ^{13}C NMR data and UV spectra (Tables 1-3), compounds (II)-(V) exist only in the open diene form



R = Me, R' = OMe (II); R = Ph, R' = OEt (III); R + R' = CH_2—CMe_2—CH_2 (IV); R = R' = OMe (V).

The configuration of the α,β double bond in dienones (II) and (III) was determined on the basis of the spin–spin interaction constants (SSIC) of the carbonyl carbon (cf. [6, 7]) in the ^{13}C NMR spectrum (Table 3).

In dienone (III) the SSIC are $^3J_{PhCO,H_\beta}$ = 8.6 and $^3J_{EtOCO,H_\beta}$ = 7.5 Hz; consequently, compound (III) is an E isomer, in which COPh and H_β are in the trans position.

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TABLE 1. Synthesis and Properties of Fluorine-Containing Compounds

Compound	Reactions conditions*		Yield, %	Mp, °C	Mol. mass (mass spectrum), found	UV spectrum λ_{max}, nm (ε)		Empirical formula	Found/Calculated, %			
	T, °C	time, h				$CHCl_3$	EtOH		C	H	N	F
(II)	20	0,5	94	127–128	215	380(44630)	387(49615)	$C_{10}H_{14}NO_3F$	55,93 55,81	6,86 6,51	6,43 6,51	8,8 8,83
(III)	20	1	78	121–122	291	364	250(13030) 370(31270)	$C_{16}H_{18}NO_3F$	66,52 65,98	6,12 6,18	4,71 4,81	–
(IV)	20	48	10	128–131	239	442,5	429(60750)	$C_{13}H_{18}NO_2F$	–	–	–	–
(V)	20	0,5	82	129–130	231	362(42465)	369(52245)	$C_{10}H_{14}NO_4F$	52,55 51,94	6,42 6,06	6,07 6,06	–
(X)	80	1	41	>280	282	498(49565)	510 **	$C_{15}H_{20}N_2OF_2$	63,42 63,83	7,32 7,09	–	–
(XI)	110–115	0,25	64	174–176	296	474(54130)	490 **	$C_{16}H_{22}N_2OF_2$	65,01 64,86	7,42 7,43	–	13,02 12,83
(XIII)	100–105	0,25	48	182–184	278	467	488(64154)	$C_{16}H_{23}N_2OF$	69,18 69,06	8,45 8,27	–	6,96 6,83
(XIV)	105–110	0,25	74	178–180	256	258(17500) 467(77475)	481 **	$C_{13}H_{18}N_2OF_2$	–	–	10,80 10,94	14,89 14,84
(XVI)	105–110	0,25	66	156–158	238	459	476(78150) 380(12433) 253(8880)	$C_{13}H_{19}N_2OF$	65,51 65,54	8,14 7,98	–	7,20 7,98

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*To obtain compounds (II), (IV), and (V) the reaction was carried out in abs. ether; in other cases it was carried out without solvent.

**ε was not determined (because of poor solubility in EtOH).

TABLE 2. PMR Spectra of Synthesized Compounds

Compound	δ, ppm										J, Hz
	H_α	$H_{\alpha'}$	H_β	$H_{\beta'}$	H_γ	H_δ	$H_{\delta'}$	OMe	COMe	NMe_2	ring protons	
Z-(II) *			6,85			6,05		3,82	2,21	3,09		$J_{H_\beta, F} = 33,0$, $J_{H_\delta, F} = 26,5$, $J_{Me_2N, F} = 1,5$
E-(II)			6,79			5,92		3,73	2,40	3,02		$J_{H_\beta, F} = 33,6$, $J_{H_\delta, F} = 25,9$, $J_{Me_2N, F} = 1,5$
(III) **			7,1			5,9				2,94		$J_{H_\beta, F} = 33,0$, $J_{H_\delta, F} = 27,0$, $J_{CH_2, CH_3} = 7,0$
(IV) ***			8,0			7,15				2,87	2,34	$J_{H_\beta, F} = 15,11$, $J_{H_\delta, F} = 21,5$
(V)			6,9			5,88		3,73 3,80		3,04		$J_{H_\beta, F} = 33,0$, $J_{H_\delta, F} = 26,9$, $J_{Me_2N, F} = 1,5$
(X)			6,65	6,65		5,7	5,7			2,97 2,98	2,82	$J_{H_\beta, F} = J_{H_{\beta'}, F} = 36,01$, $J_{H_\delta, F} = J_{H_{\delta'}, F} = 27,92$, $J_{NMe_2, F} = 1,68$
(XI)			6,9	6,9		5,7	5,7			2,95 2,96	1,68, 2,78	$J_{H_\beta, F} = J_{H_{\beta'}, F} = 37,0$, $J_{H_\delta, F} = J_{H_{\delta'}, F} = 27,5$
(XIII)			7,46	6,91	5,08	6,72	5,67			2,89 2,95	1,72, 2,57 t 2,81 t	$J_{\beta, \gamma} = J_{\gamma, \delta} = 12,5$, $J_{H_{\beta'}, F} = 37,5$, $J_{H_{\delta'}, F} = 28,1$
(XIV)	6,11	6,11	6,98	6,98		5,67	5,67			3,0		$J_{\alpha, \beta} = J_{\alpha', \beta'} = 15,0$, $J_{H_\beta, F} = J_{H_{\beta'}, F} = 30,5$, $J_{H_\delta, F} = J_{H_{\delta'}, F} = 28,0$
(XVI)	5,95	6,12	7,38	6,94	5,15	6,68	5,6			2,85 2,96		$J_{\alpha, \beta} = J_{\alpha', \beta'} = 15,0$, $J_{\gamma, \delta} = 13,0$, $J_{\beta, \gamma} = 11,0$, $J_{\beta' F} = 29,8$; $J_{H_{\beta'}, F} = 27,7$
(XVIII) ****			8,18	6,66	6,08	7,7	6,98			3,14 s 3,3 br.s	1,65 m 2,37 t 2,65 t	$J_{H_{\beta'} F} = 37,2$, $J_{H_{\delta'}, F} = 28,7$, $J_{\beta, \gamma} = 11,5$, $J_{\gamma, \delta} = 13,5$

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*Signals were assigned to E and Z isomers on the basis of the ^{13}C NMR spectrum (Table 3); E:Z = 1:3; the assignment of signals to β and δ in compounds (II), (III), and (V) was on the basis of $^{13}C-\{^1H\}$.

**The spectrum also contains the following signals (δ, ppm): 4.1 q (OCH_2), 1.08 t ($\underline{CH_3}CH_2$, $J_{CH_3CH_2}$ = 7 Hz), 7.45-7.92 (C_6H_5).

***The spectrum contains a signal at 1.05 ppm (CH_3).

****In DMSO; the spectrum contains the following signals (δ, ppm): 3.85 q (OCH_2), 1.37 t ($\underline{CH_3} \cdot CH_2$), J_{CH_3,CH_2} = 7 Hz).

TABLE 3. ^{13}C NMR Spectra of Compounds (II), (III), and (V) in $CDCl_3$ at ~25°C (δ, ppm, ($^1J_{^{13}C,^1H}$), [$J_{^{13}C,F}$], Hz)

Compound	CO	Me(Ph)	COO	OMe (OEt)	C_α	C_β	C_γ	C_δ	NMe_2
Z-(II)	192,3 (5,9 d)**	26,37 (127,6 q)	169,83 (11,0 d)	51,91 (146,5 q)	118,71	134,21 (165,4 d) [13,4 d]	136,69 [230,3 d]	136,33 * [6,1 d]	42,66 (136,7 q) [6,1 d]
E-(II)	201,0 (8,7 d)**	31,0 (127 q)	166,0 (7,5 d)	51,46 (146,5 q)	117,0	132,7	137,5 [228,2 d]	132,7	42,31 (137,3 q) [6,1 d]
(III)	195,4 (8,6 d)**	128,3 129,0 132,5 138,4	166,0 (7,5 d)	60,3 (147,0 t) 14,2 (127 q)	115,7	135,1 (156,0 d) [14,8 d]	137,5 [231,0 d]	134,1 (165 d) [4,0 d]	42,4 (135 q) [5,6]
(V)			168,22 165,60	52,12 (147,1 q) 51,73 (147,1 q)	109,41	135,0 (151,4 d) [14,0 d]	136,85 [230,0 d] (8,5 t)	134,68 (165,7 d) [5,0 d]	42,53 (138,9 q) [5,7 d]

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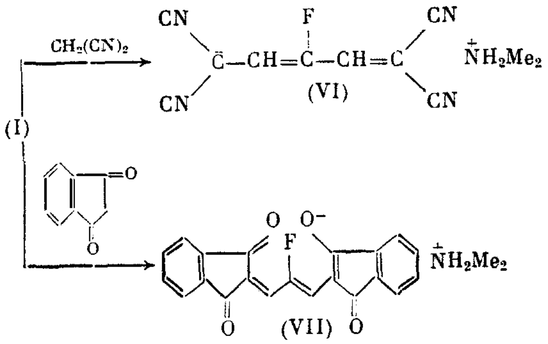
*$^1J_{^{13}C^1H}$ was not determined because of overlap.

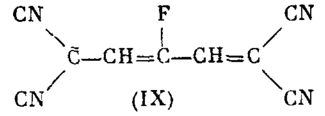
**J_{CO}, H_β

Dienone (II) is a mixture of E and Z isomers (1:3 ratio),* in which the SSIC are equal to 8.7 and 5.9 Hz, respectively, and $^3J_{MeOCO,H_\beta}$ equal 7.5 and 11.0 Hz. Since stereochemical conditions favorable for cyclization (the presence of E isomers) are present in compounds (II) and (III), the absence of a 2H-pyran form in these dienones as well as in compound (IV) may be explained by the fact that introducing a fluorine atom, which has a small Van der Waals radius (1.35 Å), into the γ-position does not produce steric hindrance, destabilizing the dienone form, as would be the case with more bulky substituents (Me, Cl, or Ph) [3-5].

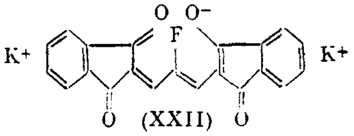
Diester (V) does not contain a 2H-pyran form, since diene esters always have an open form [8]. Unlike the condensation of aminal (I) with β-dicarbonyl compounds, which yielded δ-aminodienones, the reaction of (I) with malononitrile and indandione afforded anionic dyes (VI) and (VII) in yields of over 90%.



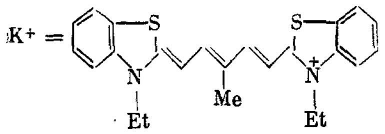
Cation $\overset{+}{N}H_2Me_2$ in compounds (VI) and (VII) is easily exchanged for a cyanin dye cation. Thus cation–anion dyes (IX) and (XXII) were obtained from Ts^-K^+(VIII).



(IX)

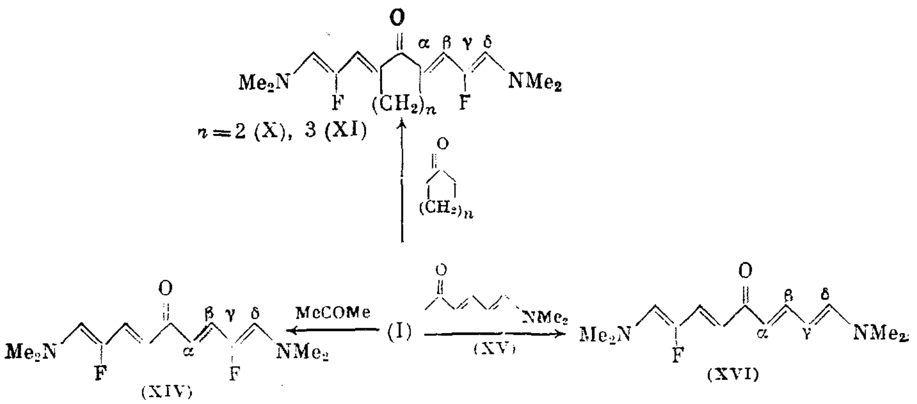


(XXII)



The electronic spectra of compounds (IX) and (XXII) contain two absorption bands corresponding to the cationic and anionic components.

When aminal (I) was condensed with cyclic and acyclic ketones at a molar ratio of 2:1 in the absence of solvent, ketocyanins (X), (XI), and (XIV), containing two fluorine atoms (in the γ- and γ'-positions), were formed readily.



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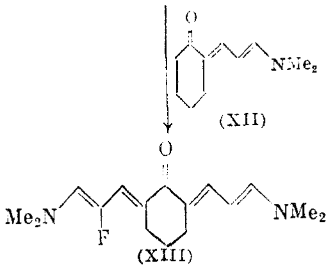
*The ratio was determined from the PMR spectrum.

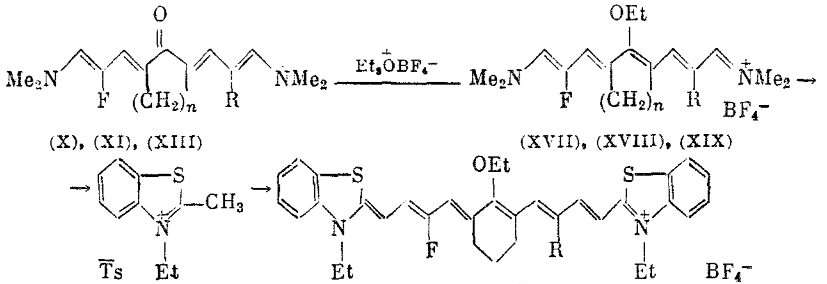


(XII)

(XIII)

To obtain ketocyanins (XIII) and (XVI), containing only one fluorine atom, we condensed the previously synthesized δ-aminodienones (XII) and (XV) with compound (I) [9].

Alkylation of ketocyanins (X), (XI), and (XIII) with $Et_3O^+BF_4^-$ in a manner analogous to that described in [10] afforded ethoxynonamethine salts (XVII)-(XIX) in high yields. Salts (XVII) and (XVIII) were used to synthesize fluorine-substituted thiapentacarbocyanin dyes (XX) and (XXI).



(X), (XI), (XIII)

(XVII), (XVIII), (XIX)

(XX), (XXI)

R = F (X), (XI), (XVII), (XIX), (XX); H (XIII), (XVIII), (XXI); $n = 2$ (X), (XIX); 3 (XI), (XIII), (XVII), (XVIII).

An analog of these dyes that does not contain fluorine atoms in the polymethine chain was obtained by us earlier [11] by condensing the appropriate alkoxynonamethine salt with 2-methyl-3-ethylbenzthiazole toluenesulfonate in acetic anhydride in the presence of triethylamine at 20°C. Thiapentacarbocyanin (XXI) was synthesized from nonamethine salt (XVIII, n = 3) under the same conditions. However, when we attempted to synthesize dye (XX) in this manner, the original alkoxynonamethine salt (XVII, n = 3) was completely decomposed. Thiapentacarbocyanin (XX), with two fluorine atoms in the polymethine chain, was successfully synthesized in acetic anhydride in the presence of dicyclohexylethylamine at 0°C in a yield of 30%.

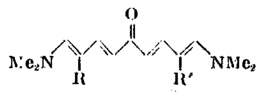
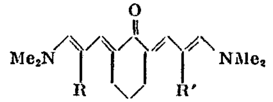
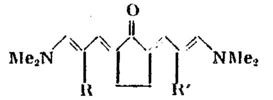
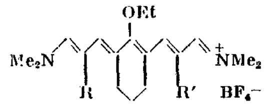
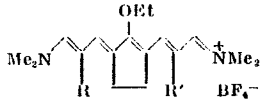
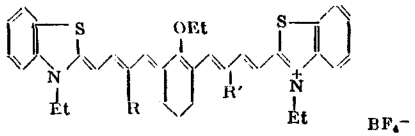
Comparative data from the electronic spectra of all the synthesized compounds and their unsubstituted analogs are presented in Tables 4 and 5.

The presence of a fluorine atom in the polymethine chain has a strong effect on the color of the dye. The introduction of fluorine atoms into even positions of the polymethine chromophore shifts the absorption band to longer wavelengths, whereas their introduction into odd positions elicits a hypsochromic shift of the absorption maximum [2]. Thus, a fluorine atom in the polymethine chain behaves like an electron donor substituent, in accordance with the Forster—Dewar—Notta (FDN) rule. The absolute value of the electron acceptor inductive effect of the fluorine atom ($\sigma_I = 0.51$) is greater than its electron donor resonance effect ($\sigma_R = -0.32$); however, according to the correlation equation [12], the resonance effect on dye color predominates.

Symmetric dyes of types (1)-(8), with fluorine atoms in even positions of the polymethine chain, have a deeper color than their unsubstituted analogs. The effect of fluorine atoms in ionic dyes of types (4)-(8) is significantly greater than in anionic merocyanins, which is associated with a smaller charge alternation along the conjugated chain in compounds (1)-(3). Two fluorine atoms in even positions have a stronger effect on dye color than one atom. Here the symmetric structure of difluoro-substituted dyes is manifested.

In unsymmetric merocyanins (9), (10), and (12) the fluorine atom elicits a hypsochromic shift of the absorption maximum, which is not consistent with the FDN rule.

TABLE 4. Electronic Spectra of Fluorine-Containing Compounds and Their Unsubstituted Analogs, Types (1)-(6)

Compound	Formula	λ_{max},* nm					
		EtOH			CHCl$_3$		
		R=R′=H	R=R′=F	R=H; R′=F	R=R′=H	R=R′=F	R=H; R′=F
(1)		472	481 (+9)	476 (+4)	455	467 (+12)	459 (+4)
(2)		485	490 (+5)	488 (+3)	463	474 (+11)	467 (+4)
(3)		504	510 (+6)	–	480	498 (+8)	–
(4)		629	666 (+37)	642 (+13)	632	664 (+32)	648 (+16)
(5)		629			625 **	666 ** (+41)	
(6)					1012 **	1076 ** (+54)	1022 ** (+10)

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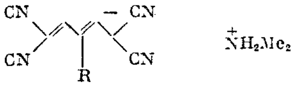
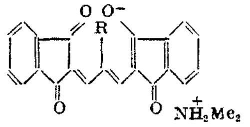
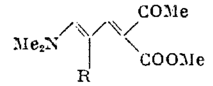
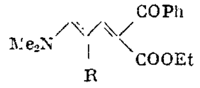
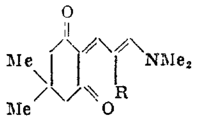
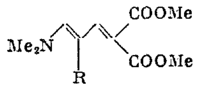
*The value of $\Delta\lambda_{max}$, compared with the unsubstituted analog, is shown in parentheses.

**In CH_2Cl_2.

TABLE 5. Electronic Spectra of Fluorine-Containing Compounds and Their Unsubstituted Analogs, Types (7)-(12)*

Compound	Formula	λ_{max}, nm			
		EtOH		CHCl$_3$	
		R=H	R=F	R=H	R=F
(7)		440	453 (+13)		
(8)		555	583 (+28)	561	587 (+26)
(9)		394	387 (−7)	394	380 (−14)
(10)		406	370 (−36)	400	364 (−36)
(11)		408	429 (+21)	416	442 (+26)
(12)		377	369 (−8)	373	362 (−11)

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*The value of $\Delta\lambda_{max}$, compared with the unsubstituted analog, is shown in parentheses.

This fact may be explained as follows. Even in unsubstituted merocyanins (9), (10), and (12), in which R = H, there are steric interactions between the electron acceptor group at C_α (which is in the trans position with respect to H_β) and proton H_γ, which causes a significant deviation of this group from the plane of the diene system. Thus, according to x-ray diffraction analysis [13], in (12, R = H) one COOMe group deviates from the plane by 41°. When, instead of H, a substituent is present in the γ-position of compound (12), this deviation is even greater, which produces a hypsochromic shift of λ_{max} compared with compound (12, R = H): 7 (R = Me), 7 (R = OEt), 17 (R = Br), 15 (R = Cl), 39 nm (R = CN).

EXPERIMENTAL

Electronic absorption spectra were measured on Specord and SF-20 instruments. PMR spectra were measured on a Bruker WM-250 instrument with a working frequency of 250 MHz on ^{1}H nuclei. High-resolution ^{13}C NMR and ^{13}C–{H} spectra were recorded on a Bruker WM-250 spectrometer with a working frequency of 62.89 MHz on ^{13}C nuclei. Aminal (I) was obtained according to the method described in [1]. Iodides K_3, K_4, and K_6; chloride K_5; and tosylates K_1 and K_2 were purified by crystallization from EtOH. Tosylates were obtained from iodides by the action of p-$MeC_6H_4SO_3Me$.

Merocyanins (II)-(V). The reaction conditions, constants, and yields of the compounds are presented in Table 1. An equimolar mixture of CH-acid and aminal (I) was allowed to stand at 20°C; the crystalline residue was separated and recrystallized from MeOH. Compound (IV) was allowed to stand for 48 h, and ether was evaporated from the reaction mass. Absolute benzene was added to the residue, and the mixture was boiled for 2 h and then evaporated. Absolute ether was then added, the mixture was cooled, and the precipitate [compound (IV)] was separated.

1,1,5,5-Tetracyano-3-fluoropenta-1,3-diene Dimethylammonium Salt (VI). A 0.45-g portion (2.3 mmoles) of compound (I) was added to a supension of 0.3 g (4.5 mmoles) $CH_2(CN)_2$ in 5 ml abs. benzene; the mixture was kept for 0.5 h at 20°C and was then evaporated. A 5-ml portion of $CHCl_3$ was added to the crystalline residue; the crystals were thoroughly ground, and the precipitate was separated and washed with $CHCl_3$. Half a gram (90%) of compound (VI), mp 107-110°C, was obtained. Found: C 54.20; H 4.97; H_2O 5.95%. $C_{11}H_{10}N_5 \cdot 0.8\ H_2O$. Calculated: C 53.65; H 4.73; H_2O 6.1%. UV spectrum (λ_{max}, nm (ε) EtOH): 453 (105080). PMR spectrum (CD_3OD, δ, ppm): 2.63 (6H, NMe_2), 6.65 (2H, CH, $J_{CH,F}$ = 30.5 Hz).

Cation–Anion Dye (IX). A solution containing 0.04 g of compound (VI) in 3 ml EtOH was added to a filtered solution of 0.1 g tosylate (VIII) in 10 ml EtOH. The mixture was kept for 3 h at 0°C; the residue was then filtered and washed with water, EtOH, and ether. After drying, 0.08 g (80%) of compound (IX) was obtained as a violet residue with a mp of 224-225°C. Absorption spectrum (λ_{max}, nm (ε), EtOH): 453 (114,000), 652 (236,000). Found: C 67.19; H 4.62; N 14.05%. $C_{33}H_{28}N_6S_2F$. Calculated: C 67.0; H 4.73; N 14.20%.

γ-Fluorotrimethinoxanine Dimethylammonium Salt (VII). A 0.12-g portion of compound (I) was added to 0.2 g indandione in 0.5 ml abs. MeOH. After 30 min the precipitate was filtered and washed with abs. ether. A 0.2-g yield (95%) of compound (VII) was obtained; mp 117-119°C (from MeOH). Electronic spectrum [λ_{max}, nm (ε)] in $CHCl_3$, 253 (41,540), 587 (102,000); in EtOH, 250 (51000), 583 (148750). PMR spectrum ($CDCl_3$, δ, ppm): 2.97 (6H, NMe_2), 7.08 (2H, H_β and H_δ), 7.55-7.67 (8H, Ph, $J_{H,F}$ = 37.1 Hz). Found: C 70.62; H 4.94; N 3.63%. $C_{23}H_{18}NO_4F$. Calculated: C 70.58; H 4.60; N 3.58%.

Cation–Anion Dye (XXII). A solution of 0.048 g of compound (VIII) in 3 ml EtOH was added to 0.035 g of compound (VII) in 3 ml EtOH. After cooling to 0°C, 0.01 g of compound (XXII) was isolated. The mother liquor was evaporated, and the residue was dissolved in 3 ml MeOH and cooled. An additional 0.014 g of compound (XXII) was isolated. Yield, 50%; mp 140-142°C (from MeOH). Electronic spectrum (λ_{max}, nm (ε), EtOH): 583 (173,000), 652 (157000).

Ketocyanin Dyes (X), (XI), (XIII), (XIV), and (XVI). The reaction conditions, yields, constants, and electronic spectral data of these dyes are presented in Table 1. To obtain compounds (X), (XI), and (XIV), 1 mole of the original ketone was heated with 2 moles of compound (I); to obtain compounds (XIII) and (XVI), an equimolar mixture of compound (I) and δ-aminodienone (XII) or (XV) was heated. The dyes were isolated by adding abs. ether to the crystalline reaction mass, separating the precipitate, and recrystallizing from ether–acetone (1:1).

Tetrafluoroborates (XVII), (XVIII), and (XIX). A 0.4-g portion of $Et_3O^+BF_4^-$ in 2 ml dry CH_2Cl_2 was gradually added at –3 to –5°C with mixing to 0.5 g of ketocyanin dye (X), (XI), or (XIII) in 5 ml dry CH_2Cl_2; the temperature was adjusted to 20°C, and the solvent was evaporated in a vacuum. Absolute ether was added to the residue, and the precipitate was separated and washed with abs. ether. Compound (XVIII) was obtained in a yield of 90%; mp 165-168°C; λ_{max} (ε) in $CHCl_3$, 648 (106,700); in EtOH, 642 nm. The PMR spectrum of compound (XVIII) is shown in Table 2. Compound (XVII) was obtained in a yield of 92%; mp 85°C with decomposition; λ_{max} (ε) in $CHCl_3$, 664 (159,800); in EtOH, 666 nm. Compound (XIX) was obtained in a yield of 90%; mp 90°C with decomposition; λ_{max} (ε) in CH_2Cl_2, 666 nm (110,880).

2-[11-(3-Ethylbenzthiazolinylidene-2)-3,9-difluoro-6-ethoxy-5,7-trimethyleneundecapentaen-1,3,5,7,9-yl-1]-3-ethylbenzthiazole Tetrafluoroborate (XX). A mixture of 0.08 g (0.2 mmole) of tetrafluoroborate (XVII, n = 3) and 0.20 g (0.6 mmole) of 2-methyl-3-ethylbenzthiazole tosylate was added to 0.08 g (0.4 mmole) of dicyclohexylethylamine in 2 ml Ac_2O. The reaction mass was mixed and kept on ice for 10 min. The precipitate was filtered; washed with a small amount of Ac_2O, ether, and water; washed again with ether; and dried. After washing the dye by mixing with Ac_2O and then with CH_2Cl_2, 0.04 g (30%) of compound (XX), in the form of small brown crystals, was obtained; mp 254-255°C with decomposition; λ_{max} in CH_2Cl_2, 1076 nm. Found: C 60.19; H 5.38; N 4.47%. $C_{34}H_{35}BF_6N_2OS_2$. Calculated: C 60.35; H 5.21; N 4.14%.

2-[11-(3-Ethylbenzthiazolinylidene-2)-3-fluoro-6-ethoxy-5,7-trimethylene-undecapentaen-1,3,5,7,9-yl-1]-3-ethylbenzthiazole Tetrafluoroborate (XXI). A 0.8-ml portion of 1 M NEt_3 in Ac_2O was added dropwise to 0.08 g (0.2 mmole) of tetrafluoroborate (XVIII, n = 3), 0.35 g (1 mmole) 2-methyl-3-ethylbenzthiazole tosylate, and 2 ml Ac_2O. The reaction mass was kept at room temperature for 25 min. The crystals formed were then filtered; washed with

Ac_2O, ether, water, and again with ether; and dried. After washing the dye by mixing with CH_2Cl_2, 0.04 g (30%) of compound (XXI), in the form of small brown crystals, was obtained; mp 248-249°C with decomposition; λ_{max} in CH_2Cl_2, 1022 nm. Found: C 62.00; H 5.69; S 9.58%. $C_{34}H_{36}BF_5N_2OS_2$. Calculated: C 62.09; H 5.52; S 9.75%.

CONCLUSIONS

1. The condensation of α-fluoro-β-dimethylaminoacrolein aminal with ketones, β-dicarbonyl compounds, and CH-acids was investigated.

2. The synthesized dimethylamino-γ-fluorodienones (merocyanins) exist in the open form and are not cyclized to 2H-pyrans.

3. γ-Fluoro and γ,γ'-difluoroketocyanins were synthesized; their alkylation afforded alkoxynonamethine salts. Fluorine-containing thiapentacarbocyanin dyes were obtained from the latter compounds.

4. Dimethylammonium salts of tetracyano-γ-fluoropentadiene and γ-fluorotrimethinoxanine were synthesized. These compounds were used as the anionic components in obtaining cation—anion cyanin dyes.

5. The effect of the fluorine atom on the color of the synthesized dyes was investigated. It was shown that a fluorine atom in the polymethine chain behaves like an electron donor substituent. However, in sterically hindered merocyanins it elicits a hypsochromic shift of the absorption band even at even positions of the polymethine chain.

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