QUINALDINE DERIVATIVES WITH FLUORINE-CONTAINING SUBSTITUENTS AND CYANINE DYES BASED ON THEM

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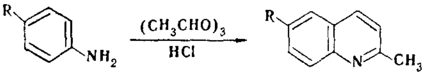
Condensation of fluorine-containing anilines with paraldehyde gave quinaldine derivatives with CF_3, CF_3S, and CF_3SO_2 groups in the 6 position, from which carbocyanine, merocyanine, and styryl dyes were synthesized. Fluorine-containing groups lower the basicity of quinaldine by 0.7-2.0 pK_a units and lead to deepening of the color of the dyes.

In a previous communication [1] we described the synthesis of fluorine-containing lepidines and cyanine dyes based on them. The aim of the present research was to obtain quinaldine derivatives with electron-acceptor trifluoromethyl, trifluoromethylthio, and trifluoromethylsulfonyl groups (II-IV) and to ascertain their effect on the color of quino(2)cyanines. The previously undescribed II-IV, as well as 6-fluoroquinaldine (I), were synthesized by condensation of the corresponding p-substituted anilines with paraldehyde by a modified method [2].



I–IV

I R=F; II R=CF_3; III R=CF_3S; IV R=CF_3SO_2

As one should have expected, I-IV are weaker bases than quinaldine. With respect to decreasing basicity they are arranged in the order H > F > CF_3S > CF_3 > CF_3SO_2, which is similar to the order established for the corresponding fluorolepidines (Table 1). The bases are crystalline substances that are quite soluble in organic solvents.

Compounds I-IV were converted by the usual methods to quaternary salts, from which symmetrical trimethylidynecyanines (V-VIII), merocyanines (IX-XI), and styryls (XII-XV, Table 2) were obtained.

The introduction of a fluorine atom and the indicated fluorine-containing substituents gives rise to a bathochromic shift of the absorption maximum of the carbocyanine dyes (V-VIII, Table 2), particularly in the case of trifluoromethylthio and trifluoromethylsulfonyl groups (12 and 18 nm, respectively). In the case of styryl dyes XII-XV the introduction of electron-acceptor CF_3, CF_3S, and CF_3SO_2 groups in the 6 position of the quinoline ring also leads to deepening of the color of the dyes; this is explained by equalization of the boundary structures of the unsymmetrical styryl dyes. This is confirmed by the decrease in the deviation of the absorption maxima of the dyes as the electron-acceptor properties of the substituents increase. Merocyanine dyes IX-XI have positive solvatochromism, and this constitutes evidence for predominance of the boundary nonpolar structure in the ground state.

TABLE 1. Fluorine-Containing Quinaldines

Compound	R	mp, °C	pK_a in 50% alcohol*	Empirical formula	F, %		Yield, %	mp of the picrates, °C
					found	calc.		
I	F	58—59[2]	3,85	$C_{10}H_8FN$	—	—	37	196
II	CF_3	65—66	3,22	$C_{11}H_8F_3N$	27.0	27.0	34	206
III	CF_3S	88	3,37	$C_{11}H_8F_3NS$	23,2	23,4	27	172
IV	CF_3SO_2	96	2,51	$C_{11}H_8F_3NO_2S$	20,8	20,7	5,4	—

*The pK_a of quinaldine under these conditions is 4.59.

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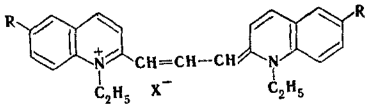
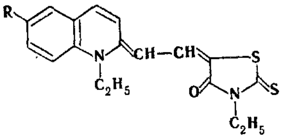
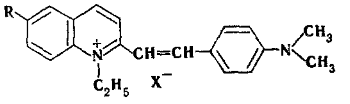
TABLE 2. Cyanine Dyes from Fluorine-Containing Quinaldines

Compound	R	mp, °C (dec.)	λ_{max}, nm, in alcohol ($\varepsilon \cdot 10^{-4}$)^a	Empirical formula^b	F, % found	F, % calc.	Yield, %
			605 (18,2)				
V	F	264	612 (15,6)	$C_{32}H_{30}F_2N_2O_3S$	7,1	6,8	57
VI	CF_3	300	608 (15,8)	$C_{27}H_{23}F_6IN_2$	18,4	18,5	30
VII	CF_3S	278	617 (15,6)	$C_{34}H_{30}F_6N_2O_3S_3$	15,7	15,7	42
VIII	CF_3SO_2	286	623 (15,2)	$C_{34}H_{30}F_6N_2O_7S_3$	14,3	14,5	26
			568 (8,75) 535 (8,0)				
IX	F	292	542; 572	$C_{18}H_{17}FN_2OS_2$^{c}			48
X	CF_3	284	537; 570	$C_{19}H_{17}F_3N_2OS_2$^{d}			52
XI	CF_3S	296	536; 568	$C_{19}H_{17}F_3N_2OS_3$	12,9	12,9	70
			527 (6,0)				
XII	F	249	536 (6,5)	$C_{28}H_{29}FN_2O_3S$^{e}			36
XIII	CF_3	261	556 (5,0)	$C_{22}H_{22}F_3IN_2$	11,5	11,4	64
XIV	CF_3S	258	558 (3,8)	$C_{22}H_{22}F_3IN_2S$	11,3	10,7	56
XV	CF_3SO_2	247	586 (2,7)	$C_{22}H_{22}F_3IN_2O_2S$	9,9	10,1	32

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[a] The corresponding λ_{max} ($\varepsilon \cdot 10^{-4}$) values for the corresponding dyes with R = H are indicated beside the structural formulas. [b] In the case of V, VII, VIII, and XII, X = p-$CH_3C_6H_4SO_3$; X = I for VI and XIII-XV. [c] Found: N 7.5%. Calculated: N 7.8%. [d] Found: N 6.7%. Calculated: N 6.8%. [e] Found: N 5.6%. Calculated: N 5.7%.

TABLE 3. Absorption Spectra of Merocyanines IX-XI in Organic Solvents

Compound	λ_{max}, nm ($\varepsilon \cdot 10^{-4}$) CCl$_4$	C_6H_6	C_2H_5OH	CH_3OH
IX	513; 544	538; 558	542; 572 (7,0; 6,2)	545; 574
X	503; 530	505; 534	537; 570 (6,6; 5,0)	536; 570
XI	506; 532	508; 532	536; 568 (7,3; 5,6)	536; 566

EXPERIMENTAL

The electronic absorption spectra of the compounds were recorded with an SF-10 spectrophotometer. The pK_a values of quinaldine and I-IV in 50% alcohol were determined by potentiometric titration at 25°C with an LPU-01 potentiometer.

p-Trifluoromethyl-, p-Trifluoromethylthio-, and p-Trifluoromethyl-sulfonylanilines. These compounds were obtained by the method in [3].

6-Trifluoromethylquinaldine (II). A mixture of 16 g (0.1 mole) of p-trifluoromethylaniline, 16 ml (0.12 mole) of paraldehyde, 16 ml of concentrated HCl, and 4 g (0.03 mole) of zinc chloride was allowed to stand at 25°C for 2 h, after which it was refluxed gently for another hour. It was then made alkaline with sodium carbonate solution and subjected to steam distillation. The distillate was extracted with ether, the ether was removed from the extract by distillation, and the residue was heated with an equal amount of acetic anhydride at 125°C for 1.5 h. The mixture was made alkaline with sodium carbonate and subjected to steam distillation. The distillate was extracted with ether, the extract was dried with anhydrous magnesium sulfate, the ether was removed by distillation, and the residue was recrystallized from petroleum ether.

Compounds III and IV (Table 1) were similarly obtained. 6-Fluoroquinaldine (I) was obtained by the method in [2].

1-Ethyl-6-R-Quinaldinium Toluenesulfonates. These compounds were obtained by heating the corresponding bases with an equimolar amount of ethyl p-toluenesulfonate at 130-140°C for 4 h, after which the cooled mixture was washed with ether and dissolved in hot water. The aqueous solution was washed with toluene and subjected to partial evaporation. The concentrate was cooled, and the precipitated crystals of the quaternary salt were removed by filtration. The products were air dried, dissolved in methanol, and precipitated by the addition of ether (yields and melting points given): $R = F$ (46; 186), $R = CF_3$ (62; 193), $R = CF_3S$ (58; 196), and $R = CF_3SO_2$ (54; 218). The results of analysis of the toluenesulfonates for their fluorine content were in agreement with the calculated values.

$6,6^1$-R_2-$1,1^1$-Diethyl-$2,2^1$-carbocyanines (V-VIII, Table 2). A mixture of 1 mmole of 1-ethyl-6-R-quinaldinium toluenesulfonate, 0.33 ml (2 mmole) of ethyl orthoformate, 3 ml of pyridine, and four to five drops (~ 2 mmole) of triethylamine was refluxed for 50 min. The next day the dye crystals were removed by filtration, washed with a small amount of alcohol and ether, and recrystallized from methanol. Dye VI was isolated from the reaction mixture in the toluenesulfonate form. The anion was then replaced by iodide ion by means of an aqueous alcohol solution of potassium iodide.

6-R-Quino(2)dimethylidynemerocyanines – 3-Ethylrhodanine Derivatives (IX-XI, Table 2). A mixture of 1 mmole of the corresponding quaternary salt, 0.27 g (1 mmole) of 3-ethyl-5-acetanilidomethylenerhodanine, 3 ml of pyridine, and four to five drops (~ 2 mmole) of triethylamine was refluxed for 90 min. The next day the dye was removed by filtration, washed with a small amount of alcohol, and crystallized from methanol.

2-p-Dimethylaminostyryl Dyes (XII-XV, Table 2). A mixture of 1 mmole of the corresponding quaternary salt, 0.18 g (1.2 mmole) of p-dimethylaminobenzaldehyde, and 3 ml of pyridine was refluxed for 1 h. Except for XII, the dyes were isolated in the form of iodides, as in the case of VI. The products were recrystallized from methanol.

LITERATURE CITED

1. Z. Ya. Krainer, P. F. Gudz', and L. M. Yagupol'skii, Khim. Geterotsikl. Soedin., No. 2, 235 (1973).
2. M. Julian, Zeszyty Nauk. Uniw. Jagiel; Ser. Nauk Chem., 173 (1962).
3. L. M. Yagupol'skii and M. S. Marenets, Zh. Obshch. Khim., 24, 887 (1954).
4. A. I. Kiprianov and L. M. Yagupol'skii, Zh. Obshch. Khim., 22, 2209 (1952).