FLUORINE-CONTAINING LEPIDINES AND CYANINE DYES BASED ON THEM

Z. Ya. Krainer, P. F. Gudz',
and L. M. Yagupol'skii

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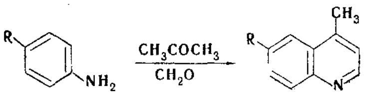
6-F-, 6-CF_3-, 6-CF_3S-, and 6-CF_3SO_2 derivatives of lepidine, their ethotosylates, and a number of carbocyanines, merocyanines, and styryl dyes were synthesized. The effect of the indicated substituents on the basicity of the heterocyclic ring and on the position of the absorption maxima of the cyanine dyes was ascertained.

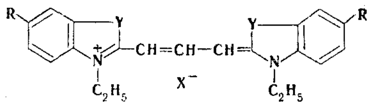
Cyanine dyes from lepidine derivatives with fluorine atoms or fluorine-containing groupings as substituents were previously unknown. It was of interest to obtain dyes of this sort and compare their properties with analogous dyes – benzothiazole and benzimidazole derivatives. It should be noted that the latter find practical application as photosensitizers. Lepidine derivatives containing a fluorine atom and CF_3, CF_3S, and CF_3SO_2 groups in the 6 position that are necessary for the synthesis of cyanine dyes have not been described. They were obtained from the corresponding substituted aniline by condensation with acetone and formaldehyde via a modification of the method in [1].



R=F, CF_3, CF_3S, CF_3SO_2

The compounds obtained are crystalline substances that are quite soluble in organic solvents and are weaker bases than lepidine. With respect to basicity, they are arranged in the order H > F > CF_3S > CF_3 > CF_3SO_2. The pK_a values in 50% alcohol, determined by potentiometric titration, are, respectively, 4.38, 3.61, 3.19, 3.08, and 2.32. The bases were converted to quaternary salts by heating with ethyl p-toluenesulfonate. Carbocyanine, merocyanine, and styryl dyes were synthesized from the ethotosylates.

TABLE 1. Shift in the Absorption Maxima of Dyes on Introduction of Substituents



Y \ R	$\Delta\lambda_{max}$, nm			
	F	CF_3	CF_3S	CF_3SO_2
S	0	3	10	17
NC_2H_5	5	3	10	21
Lepidine	7	6	19	34

The introduction of fluorine atoms and CF_3, CF_3S, and CF_3SO_2 groups into the 6,6' positions of lepidine causes a considerably greater shift in the absorption maximum of the dyes to the long-wave side as compared with the shift in the analogous dyes, benzothiazole and benzimidazole derivatives [2] (Table 1). Fluorine atoms and fluorine-containing substituents in the 6 position of the lepidine ring cause a bathochromic shift of the absorption maximum of 3-ethylrhodanine derivatives (merocyanine, Table 2). The dyes display positive solvatochromism, and this attests to predominance of the nonpolar merocyanine structure (Table 3). The effect of the indicated substituents is exerted particularly markedly on the position of the absorption maxima of the styryl dyes (Table 2). The greater the electron-acceptor properties of a substituent, the greater the shift in λ_{max}: in the case of the CF_3SO_2 group, the shift amounts to

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TABLE 2. Cyanine Dyes from Fluorine-Containing Lepidines

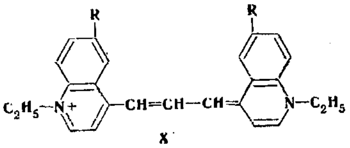
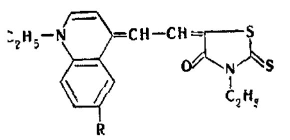
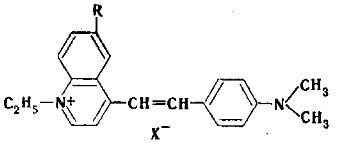
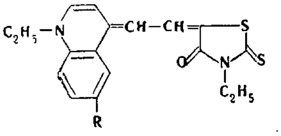
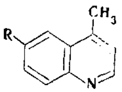
Comp.	R	X	mp, °C	λ_{max}, nm in C_2H_5OH (same without substit.)	Empirical formula	Found, %		Calc., %		Yield, %
						N	F	N	F	
										
V	F	I^-	275—276	658; 718 (650; 711)	$C_{25}H_{23}F_2N_2$	5,44	—	5,31	—	62
VI	CF_3	I^-	254—255	657; 717	$C_{27}H_{23}F_6N_2I$	—	18,23	—	18,49	22
VII	SCF_3	TOS^-	259—260	666; 730	$C_{34}H_{30}F_6O_3N_2S_3$	—	15,64	—	15,73	28
VIII	SO_2CF_3	TOS^-	274	676; 745	$C_{34}H_{30}F_6N_2O_7S_3$	—	14,39	—	14,45	46
										
IX	F		266	581; 625 (616)	$C_{18}H_{17}FN_2OS_2$	7,80	5,28	7,77	5,27	64
X	CF_3		300	579; 621	$C_{19}H_{17}F_3N_2OS_2$	6,91	13,93	6,82	13,88	52
XI	SCF_3		279	576; 618	$C_{19}H_{17}F_3N_2OS_3$	—	12,82	—	12,88	46
XII	SO_2CF_3		272	580; 618	$C_{19}H_{17}F_3N_2O_3S_3$	—	12,17	—	12,01	62
										
XIII	F	I^-	265	564 (546)	$C_{21}H_{22}F_3IN_2$	6,22	4,30	6,25	4,24	44
XIV	CF_3	I^-	237	580	$C_{22}H_{22}F_3IN_2$	—	11,45	—	11,44	72
XV	SCF_3	I^-	246	584	$C_{22}H_{22}F_3IN_2S$	5,38	10,80	5,29	10,75	70
XVI	SO_2CF_3	I^-	223	626	$C_{22}H_{22}F_3IN_2O_2S$	—	10,20	—	10,13	36

TABLE 3. UV Absorption Maxima of Merocyanines



R	λ_{max}, nm			
	CCl_4	C_6H_6	C_2H_5OH	CH_3OH
F	565, 602	575, 614	581, 625	583, 625
CF_3	563, 592	568, 606	579, 621	585, 625
SCF_3	555, 590	568, 600	576, 618	580, 621
SO_2CF_3	558	570, 608	580, 618	582, 620

TABLE 4. Fluorine-Containing Lepidines



Comp.	R	mp, °C	mp of picrates	Empirical formula	F, %		Yield, %
					found, %	calc., %	
I	F	45	231	$C_{10}H_8FN$	12,08	11,78	25
II	CF_3	56	220	$C_{11}H_8F_3N$	27,01	26,99	28
III	CF_3S	78	202	$C_{11}H_8F_3NS$	23,30	23,43	25,6
IV	CF_3SO_2	109	198	$C_{11}H_8F_3NO_2S$	20,77	20,71	6,9

80 nm. A structure with a positive charge on the nitrogen atom of the heterocyclic ring predominates markedly in the synthesized styryl dyes.

EXPERIMENTAL

p-Trifluoromethylmercapto- and p-Trifluoromethylsulfonylanilines. These compounds were obtained by the method in [3].

6-Trifluoromethyllepidine. A mixture of 27 g of ferric chloride, 8 ml of acetone, 2 ml of formalin, 4.5 ml of concentrated HCl, and 8 ml of methanol was heated at 100°, and 8.05 g (0.05 mole) of p-trifluoromethylaniline [4] was added with constant stirring after 1 h. The mixture was heated at 100° for another 3 h and under gentle reflux for 1 h. The alcohol and excess acetone were removed by distillation, and the residue was made alkaline and steam distilled. The residue was then extracted with ether, the ether was removed by distillation, and the residue was heated with acetic anhydride at 100° for 45 min. The mixture was neutralized with sodium carbonate solution and steam distilled. The residue was extracted with ether, and the extract was dried. The ether was removed by distillation, and the product was crystallized from petroleum ether.

6-Fluoro-, 6-trifluoromethylmercapto-, and 6-trifluoromethylsulfonyllepidines (Table 4) were similarly obtained.

Ethotosylates. The ethyl tosylates of the indicated bases were obtained by heating substituted lepidines with ethyl p-toluenesulfonate at 140° for 4 h. The quaternary salt was extracted with warm water, and the aqueous extract was purified by washing with toluene. The water was evaporated to a minimum volume, and the solution was allowed to stand overnight. The next day the crystals of quaternary salt were removed by filtration and dried. In the case of 6-fluorolepidine, the water was evaporated to dryness, at the end of which the mixture was heated cautiously to 140°.

Trimethylidynecyanines. A mixture of 1 mmole of the ethotosylate of the base, an equal amount by weight of ethyl orthoformate, 3 ml of pyridine, and 5 drops of triethylamine was refluxed gently for 1.5 h and allowed to stand overnight. The dyes were removed by filtration, washed with a small amount of alcohol and ether, and crystallized from methanol. Carbocyanines V and VI were converted to iodides by the action of aqueous potassium iodide solution. They were purified similarly.

Dimethylidynemerocyanines. A mixture of 1 mmole of the ethotosylate of the base, 1 mmole of 3-ethyl-5-acetanilidomethylenerhodanine, 3 ml of pyridine, and 0.1 ml of triethylamine was refluxed for 1.5 h and allowed to stand overnight. The dyes were removed by filtration, washed with a small amount of alcohol, and crystallized from methanol.

Styryl Dyes. A mixture of 1 mmole of the ethyl tosylate of the base, 1.2 mmole of p-dimethylaminobenzaldehyde, and 3 ml of pyridine was refluxed for 1 h. The dyes were converted to iodides.

LITERATURE CITED

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2. L. M. Yagupol'skii, Dissertation [in Russian], Kiev (1965).
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4. A. I. Kiprianov and L. M. Yagupol'skii, Zh. Obshch. Khim., 22, 2209 (1952).