RESEARCH IN THE POLYMEROCYANINE SERIES.

8. 4-QUINODIMEROCYANINE DYES WITH FLUORINE-CONTAINING SUBSTITUENTS

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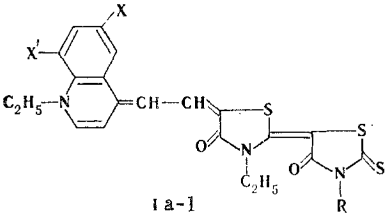
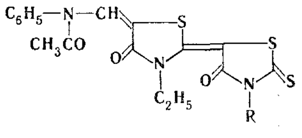
4-Quinomerocyanine dyes with fluorine-containing substituents in the 6 position of the quinoline residue were synthesized. The introduction of electronegative substituents does not have a substantial effect on the color of the dyes obtained and weakens their sensitizing action.

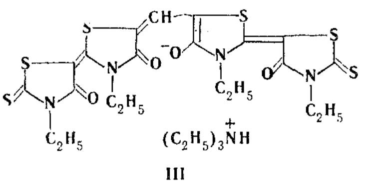
Carbocyanine, dimethylidynemerocyanine, and styryl dyes with 4-quinoline residues that are substituted in the 6 position with a fluorine atom or fluorine-containing groups have been previously synthesized, and the effect of these substituents on the color of the dyes obtained has been investigated [1, 2]. The present research was devoted to the synthesis and investigation of the properties of the analogous 4-quinodimerocyanine dyes (I). Up until now such dyes were unknown.

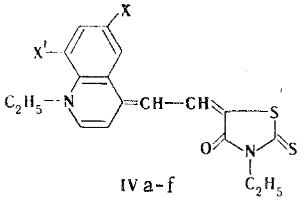

I a-l


II

X=H, F, CF_3, SCF_3, CF_3SO; X'=H, F; I a-f $R=C_2H_5$; g-l $R=(CH_2)_5COOCH(CH_3)_2$

The synthesis of Ib-l (Table 1) was accomplished by means of a previously proposed method [3] by heating quaternary salts of substituted lepidines with 5-acetanilinomethylenenullomethylidynemerocyanines (II) in pyridine in the presence of triethylamine. A 5-isopropyloxycarbonylpentyl residue was added to the nitrogen atom of rhodanine in order to increase the solubilities of the dyes in alcohol.


III


IV a-f

λ_{max} in C_2H_5OH 650 nm [4, 6], in $CHCl_3$ — 660 nm

It is known [1] that in the case of dimethylidynemerocyanines that are 3-ethylrhodanine derivatives the fluorine atom and fluorine-containing substituents in the 6 position of the 4-quinoline residue give rise to a slight (2-9 nm) bathochromic shift of the absorption maximum; a substantial change in the color (±4-6 nm) also is not observed in dimerocyanine series I (Table 1) in this case. One might have assumed that the introduction of electron-acceptor substituents in the 6 position of the quinoline residue would lead to a certain change in the electron density distribution in the chromophore of dimerocyanine Ia (X = X' = H) and brings

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TABLE 1. Dimerocyanine Dyes (I)

Compound [a]	X	mp (dec.), °C	λ_{max}, nm ($\varepsilon \cdot 10^{-4}$), in alcohol[b]	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
Ib	F	325—326	670, 620 (12,1; 7,2)	56,4	4,5	8,8	$C_{23}H_{22}FN_3O_2S_3$	56,7	4,5	8,6	53
Ic	F	325—327	660, 614 (13,2; 7,8)	54,3	4,2	8,1	$C_{23}H_{21}F_2N_3O_2S_3$	54,6	4,2	8,3	67
Id	CF_3S	298—299	665, 617 (13,3; 7,9)	50,6	4,0	7,3	$C_{24}H_{22}F_3N_3O_2S_4$	50,6	3,9	7,4	56
Ie	CF_3	327—328	660, 614 (13,6; 8,0)	53,4	4,3	7,5	$C_{24}H_{22}F_3N_3O_2S_3$	53,6	4,1	7,8	61
If	CF_3SO	299—301	665, 617 (13,8; 8,2)	—	—	7,3	$C_{24}H_{22}F_3N_3O_3S_4$	—	—	7,2	55
Ig	H	240—241	665, 616 (12,0; 7,1)	60,1	5,6	6,7	$C_{30}H_{35}N_3O_4S_3$	60,3	5,9	7,0	40
Ih	F	251—253	670, 620 (12,2; 7,2)	58,8	5,4	6,9	$C_{30}H_{34}FN_3O_4S_3$	58,5	5,5	6,8	74
Ii	F	255—257	660, 614 (13,1; 7,8)	56,9	5,5	6,4	$C_{30}H_{33}F_2N_3O_4S_3$	56,9	5,2	6,6	63
Ij	CF_3S	244,5—245	665, 618 (13,4; 7,9)	52,9	4,6	5,7	$C_{31}H_{34}F_3N_3O_4S_4$	53,3	4,9	6,0	63
Ik	CF_3	268—269	660, 614 (13,5; 8,1)	55,8	4,9	6,1	$C_{31}H_{34}F_3N_3O_4S_3$	55,9	5,1	6,3	63
Il	CF_3SO	244,5—246	665, 617 (13,7; 8,2)	—	—	5,8	$C_{31}H_{34}F_3N_3O_5S_4$	—	—	5,9	50

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[a] For Ia-f R = C_2H_5, for Ig-*l* $R_2 = (CH_2)_5COOCH(CH_3)_2$, for Ic, i X' = F, while for the remaining I X' = H. [b] For Ia: 664 and 618 nm (12.0 and 7.1) [4].

TABLE 2. Spectral Characteristics of Dyes Ia, b, d-f and IVa, b, d-f and 1,1'-Diethyl-6,6'-X_2-4-quinocarbocyaninium Iodides

X	λ_{max}, nm ($\varepsilon \cdot 10^{-4}$)					D, nm (in $C_2H_5OH/CHCl_3$)	
	I in $CHCl_3$	carbocyanines		IV			
		in C_2H_5OH	in $CHCl_3$	in C_2H_5OH	in $CHCl_3$	I	IV
H	662, 614	710 (21,0) [6]	718	618, 577 (11,5; 6,9)	620, 578	16 [4, 6]/27	7/14
F	664, 616	718 (22,2) [1]	732	625, 583 (11,7; 7,0)	625, 583	14/32	4/16
CF_3S	656, 612	730 (23,1) [1]	738	624, 580 (19,9; 7,4)	616, 576	25/43	11/28
CF_3	650, 607	717 (22,0) [1]	730	619, 577 (13,1; 7,7)	612, 572	23,5/45	9,5/28
CF_3SO	656, 612	728 (23,0)	736	624, 582 (13,3; 7,8)	616, 576	23/42	10/27

the structures of the dyes obtained close to nonpolar structures. In this connection, using the known method [5] that was previously used for the analysis of the color dimerocyanines [4, 6] we calculated the wavelengths of the absorption maxima of dyes Ia-f as the arithmetic mean values of the absorption maxima of the corresponding symmetrical carbocyanines [1] and four-ring oxanine III [4, 6] and determined the deviations (D) of the absorption maxima in alcohol and chloroform (Table 2).

For comparison, we also calculated the deviations in alcohol and chloroform of the previously described [1] dimethylidynemerocyanines IV (Table 2). The absorption maximum of the symmetrical monomethylidyneoxanine, which is a 3-ethylrhodanine derivative, that was used for this calculation appears at 540 nm in alcohol and at 550 nm in chloroform. It is apparent from Table 2 that the deviations of intraionoid compounds I and IV in chloroform, as previously established [7], more clearly (than in alcohol) characterize the effect of the substituents on the electron density distribution in the chromophore. The increase in the derivations and the positive solvatochromism observed in the series of dyes I and IV on passing from alcohol to chloroform (Table 2) constitute evidence that the introduction of electronegative substituents in the 6 position of the quinoline residue brings the structures of these compounds close to nonpolar structures.

A study of the photographic properties of dimerocyanines I showed that the introduction of fluorine atoms and fluorine-containing substituents into the quinoline ring weakens the sensitizing effect.*

EXPERIMENTAL

3-Ethyl-2-(2-thioxo-3-ω-isopropoxycarbonylpentyl-4-oxothiazolidin-5-ylidene)-5-acetanilinomethylenethiazolidin-4-one [II, R = $(CH_2)_5COOCH(CH_3)_2$]. A mixture of 2.64 g (10 mmole) of 2-thioxo-3-ethyl-5-anilinomethylenethiazolidin-4-one and 1.7 ml (18 mmole) of dimethyl sulfate was heated at 120-125°C (bath temperature) for 45 min, and the resulting quaternary salt was washed with dry ether (three 20-ml portions) and dissolved by heating in 30 ml of dry chloroform. A solution of 2.9 g (10 mmole) of 3-ω-isopropoxycarbonylpentylrhodanine in 30 ml of dry benzene and 1.4 ml (10 mmole) of triethylamine was added to a solution of the salt cooled to room temperature, and the mixture was stirred periodically for 30 min, after which it was evaporated *in vacuo*. Alcohol (20 ml) was added to the oily residue, the alcohol was removed by distillation *in vacuo*, the residue was triturated with 6 ml of alcohol, and the mixture was allowed to stand in a refrigerator for 16-20 h. The resulting orange crystals were removed by filtration and washed on the filter with 12 ml of alcohol to give 0.96 g (19%) of 3-ethyl-2-(2-thioxo-3-ω-isopropoxycarbonylpentyl-4-oxothiazolidine-5-ylidene)-5-anilinomethylenethiazolidine-4-one with mp 192-195°C. A mixture of 0.84 g (1.6 mmole) of the resulting anilinomethylenemerocyanine, 5.3 ml of acetic anhydride, and 0.07 ml (0.5 mmole) of triethylamine was refluxed for 45 min, after which it was cooled in ice, and 0.75 g (83%) of acetyl derivative II was removed by filtration. Two recrystallizations from ethanol (1:55) gave 0.56 g (63%) of orange crystals with mp 155-156°C. Found: S 17.1%. $C_{16}H_{31}N_3O_5S_3$. Calculated: S 17.1%.

1,1'-Diethyl-6,6'-bis(trifluoromethylsulfinyl)-4-quinocarbocyaninium Iodide. This compound was obtained by the method in [1] from 0.46 g (1 mmole) of 1-ethyl-4-methyl-6-trifluoromethylsulfinylquinolinium toluenesulfonate and 0.15 ml (∿1 mmole) of ethyl orthoformate by heating in 3 ml of pyridine in the presence of five drops of triethylamine with subsequent treatment with 10% potassium iodide solution. Workup gave 0.23 g (65%) of a product with mp 285-286°C (dec.). Recrystallization from methanol (1:75) gave brownish-green crystals with a bronze luster and mp 286-287°C (dec.). Found: N 3.7; S 9.3%. $C_{27}H_{23}F_6IN_2O_2S_2$. Calculated: N 3.9; S 9.0%.

2-Thioxo-3-ethyl-5-(1-ethyl-6-trifluoromethylsulfinyl-1,4-dihydroquinoline-4-ylideneethylidene)thiazolidin-4-one (IVf). This compound was obtained by the method in [1] from 0.46 g (1 mmole) of V and 0.31 g (1 mmole) of 3-ethyl-5-acetanilinomethylenerhodanine by heating in 6 ml of pyridine in the presence of 0.16 ml (1.14 mmole) of triethylamine. Workup gave 0.26 g (56%) of a product with mp 262-266°C. For purification 0.26 g of merocyanine IVf was refluxed with 50 ml of methanol, and this operation was repeated once again. The yield of product with mp 263-266°C was 0.5 g. Found: N 6.2%. $C_{19}H_{17}F_3N_2O_2S_3$. Calculated: N 6.4%.

3-Ethyl-2-(2-thioxo-3-R-4-oxothiazolidin-5-ylidene)-5-(1-ethyl-6-X-8'-1,4-dihydroquinolin-4-ylideneethylidene)thiazolidin-4-ones (Dimerocyanines I, Table 1). This compound was obtained by refluxing 0.25 mmole of the quaternary salt of substituted lepidine and 0.25 mmole of merocyanine II in 2 ml of dry pyridine in the presence of 0.04 ml (0.3 mmole) of triethylamine for 30 min. The reaction mixture was then diluted with 2 ml of alcohol and allowed to stand for 30 min at room temperature. The resulting precipitate was removed by filtration and washed with a small amount of alcohol. For purification the crude product was stirred several times with 2-5 ml of a mixture of benzene with alcohol (1:4 or 1:7) and washed on the filter with 1-2 ml of the same mixture and the same amount of alcohol.

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