

11. J. Wibaut, H. Willink, and W. Nienwenhuis, *Rec. Trav. Chim.*, **54**, 804 (1935).
12. R. Miller, *Ber.*, **21**, 1828 (1925).
13. J. Conolly, *J. Chem. Soc.*, **127**, 2085 (1925).
14. G. Mills and W. Ordich, *J. Chem. Soc.*, **47**, 86 (1928).
15. G. Clemo and A. Perkin, *J. Chem. Soc.*, **125**, 1622 (1924).

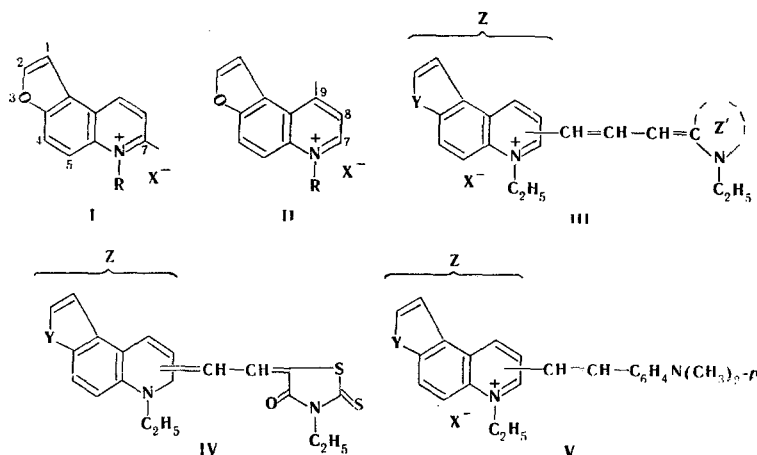
POLYMETHINE DYES - FURO[3,2-f]QUINOL-7-YL AND FURO[3,2-f]QUINOL-9-YL DERIVATIVES

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New heterocyclic bases - 7- and 9-methylfuro[3,2-f]quinolines - were synthesized by condensation of 5-aminobenzofuran double tin hydrochloride salt with paraldehyde in dilute hydrochloric acid and with methyl vinyl ketone in ethanol in the presence of ferric chloride and zinc chloride. Polymethine dyes of various types were obtained from the quaternary salts of the synthesized bases. The introduction of a furan ring in the 5,6 position of quino-2- and quino-4-carbocyanines gives rise to a smaller bathochromic effect than the analogous introduction of a thieno and, particularly, a benzo group.

It has been previously shown that the introduction of a thieno group in the 5,6 position of quino-4-carbocyanines gives rise to a smaller bathochromic effect than the analogous introduction of a benzo group. However, there is practically no difference in the color of dyes with 5,6-benzoquinol-2-yl and thieno[3,2-f]quinol-7-yl residues. In order to ascertain the effect of the analogous replacement of a vinylene group by an oxygen atom on the spectra of the dyes, we synthesized carbocyanines, merocyanines, and p-dimethylaminostyryl dyes with residues with furo[3,2-f]quinol-7-yl and furo[3,2-f]quinol-9-yl structures (I, II), respectively: III, IV, and V:



Y=O, Z'=Z= benzothiazolyl, 2-quinolyl, or 4-quinolyl, X - acid residue

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TABLE 1. Absorption Maxima (in Ethanol) of Carbocyanines, Merocyanines, and p-Dimethylaminostyryl Dyes

Compound	In formulas III-IV				λ_{max} , nm	lg ϵ	Hypsochromic shift, nm
	Y in residue Z	position of bond of the pyridine ring in Z with the polymethine chain	Y in Z' when Z' = Z or residue Z' when Z' \neq Z	position of the bond of the pyridine ring in Z' with the polymethine chain			
In formula III when Z = Z'							
VIII	CH=CH	2	CH=CH	2	635 ⁹		
IX	-S-	2	-S-	2	636 ¹		
X	-O-	2	-O-	2	626	5,24	
	CH=CH	4	CH=CH	4	736		
	-S-	4	-S-	4	729 ¹		
XI	-O-	4	-O-	4	717	5,14	
In formula III when Z \neq Z'							
XII	CH=CH	2	2-Quinoly1		616		5,0
	-O-	2	2-Quinoly1		614	5,06	2,5
XIII	-O-	4	Benzothiazoly1		631	5,25	6,5
XIV	-O-	4	2-Quinoly1		659	5,18	3,0
XV	-O-	4	4-Quinoly1		713	5,09	1,0
In formula IV							
	CH=CH	2			584		4,5
	-S-	2			584		5,0
XVI	-O-	2			580	5,03	4,0
	CH=CH	4			631		8,0
	-S-	4			625		10,5
XVII	-O-	4			623	5,14	6,5
In formula V							
XVIII	CH=CH	2			530		92,5
	-O-	2			526	4,96	92,0
	CH=CH	4			557		103,5
XIX	-O-	4			506	4,98	157,5

7- and 9-Methylfuro[3,2-f]quinolines (VI and VII) were synthesized by condensation of 5-aminobenzofuran double tin hydrochloride salt, respectively, with paraldehyde or methyl vinyl ketone in the presence of acidic agents.*

In the condensation of 5-aminobenzo[b]thiophene and 5-aminobenzo[b]furan with carbonyl compounds the new ring is usually closed in the 4 position [3-5]. The structures of VI and VII are also confirmed by their PMR spectra, which contain two doublets of 4-H and 5-H protons at 7.55 and 7.75 ppm (in the case of VI) and 7.58 and 7.78 ppm (in the case of VII) with J = 9.7 and 9.8 Hz, respectively.

To obtain symmetrical carbocyanines III, the ethiodides of VI and VII were subjected to condensation with ethyl orthoformate in nitrobenzene [6] (30-36% yields) and with ethoxymethylenemalonic ester in anhydrous ethanol in the presence of triethylamine with heating (53-67% yields) [7]. Unsymmetrical carbocyanines III and dyes IV and V were obtained by known methods for the synthesis of such compounds [8].

The data in Table 1 show that the introduction of a furan ring in the 5,6 position in quino-2- and quino-4-carbocyanines gives rise to a smaller bathochromic shift of their absorption maxima than the analogous introduction of a thieno and, particularly, a benzo group.

The furo-[3,2-f]quinol-7-yl and furo[3,2-f]quinol-9-yl derivatives also have higher colors than the corresponding dyes with thieno[3,2-f]quinol-7-yl and thieno[3,2-f]quinol-9-yl residues.

It is apparent from a comparison of the hypsochromic shifts presented in Table 1 that the basicities of the furo[3,2-f]quinol-7-yl (I) and benzo[h]quinol-2-yl residues are close to one another. However, the furo[3,2-f]quinol-9-yl (II) residue is more basic than the benzo[h]quinol-4-yl residue.

*The method differs from the method previously developed in [2].

TABLE 2. Cyanine Dyes

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	I		C	H	I	
X	>300	62.0	4.3	22.4	C ₂₉ H ₂₅ IN ₂ O ₂	62.1	4.5	22.6	30 ^a 53 ^b
XI	243—245 c	61.9	4.4	22.5	C ₂₉ H ₂₅ IN ₂ O ₂	62.1	4.5	22.6	36 ^a 67 ^b
XIII	213—215 d	56.9	4.2	24.0	C ₂₅ H ₂₃ IN ₂ OS	57.0	4.4	24.1	57
XII	259—260 e	62.1	4.6	24.3	C ₂₇ H ₂₅ IN ₂ O	62.3	4.8	24.4	44
XIV	221—222 f	62.1	4.7	24.2	C ₂₇ H ₂₅ IN ₂ O	62.3	4.8	24.4	47
XV	188—190 e	62.2	4.6	24.3	C ₂₇ H ₂₅ IN ₂ O	62.3	4.8	24.4	35
XVI	229—230 d	62.5	4.6	—	C ₂₀ H ₁₈ N ₂ O ₂ S ₂ g	62.8	4.7	—	38
XVII	209—211 d	62.6	4.6	—	C ₂₀ H ₁₈ N ₂ O ₂ S g	62.8	4.7	—	41
XVIII	254—255 d	58.7	4.9	26.8	C ₂₃ H ₂₃ IN ₂ O	58.7	5.0	27.0	34
XIX	214—215 d	58.6	4.8	26.9	C ₂₃ H ₂₃ IN ₂ O	58.7	5.0	27.0	38

^a By method A. ^b By method B. ^c Dark-green needles. ^d Dark-violet prisms. ^e Dark-blue prisms. ^f Violet prisms. ^g Found: S 16.6%. Calculated: S 16.7%.

EXPERIMENTAL

The absorption spectra of the dyes in ethanol were measured with an SF-2 spectrophotometer. The PMR spectra of carbon tetrachloride solutions of the compounds were recorded with a Varian T-60 spectrometer.

7-Methylfuro[3,2-f]quinoline (VI). Paraldehyde (15 ml) was added to a mixture of 30 g (0.05 mole) of 5-aminobenzofuran double tin hydrochloride salt and 600 ml of dilute (1:1) hydrochloric acid, and the mixture was refluxed for 1.5 h. The base was isolated by the method in [11] to give 4.4 g (48%) of a light-yellow oil with bp 155–157° (10 mm). Found: C 78.5; H 4.8; N 7.4%. C₁₂H₉NO. Calculated C 78.7; H 4.9; N 7.6%. The ethiodide was obtained as light-yellow prism (from anhydrous ethanol) with mp >300°. Found: C 49.4; H 4.0; N 4.0%. C₁₄H₁₄INO. Calculated: C 49.55; H 4.1; N 4.1%.

9-Methylfuro[3,2-f]quinoline (VII). This compound was obtained from 30 g (0.05 mole) of 5-aminobenzofuran double tin hydrochloride salt and 8 g (0.1 mole) of methyl vinyl ketone in the presence of 28 g of ferric chloride and 2 g of anhydrous zinc chloride in 200 ml of anhydrous ethanol by the method in [11]. Woukup gave 3.9 g (42.6%) of colorless prisms with mp 77–78° (from petroleum ether). PMR spectrum: 2.66 (s, CH₃), 7.02 (d, 1-H, J_{1,2} = 1.9 Hz), 7.51 (d, 2-H), 7.58 (d, 4-H), J_{4,5} = 9.8 Hz), 7.78 (d, 5-H), 8.41 (d, 7-H, J_{7,8} = 5.1 Hz), 6.52 ppm (d, 8-H). UV spectrum: λ_{max} 246 nm (log ε 4.48). Found: C 78.6; H 4.8; N 7.5%. C₁₂H₉NO. Calculated: C 78.7; H 4.9; N 7.6%. The ethiodide was obtained as light-yellow prisms (from ethanol with mp 194–195°. Found: C 49.4; H 3.9; N 4.0%. C₁₄H₁₄INO. Calculated: C 49.55; H 4.1; N 4.1%.

Symmetrical Carbocyanines X and XI (Table 2). These compounds were synthesized by condensation, respectively, of 0.34 g (0.001 mole) of ethiodide VI or VII with 0.30 g of ethyl orthoformate in 3 ml of nitrobenzene at 180–190° for 5 min (method A) and by reaction of 0.002 mole of ethiodide VI or VII with 0.0014 mole of ethoxymethylenemalonate in 3 ml of anhydrous ethanol by heating on a boiling-water bath for 40 min in the presence of 0.001 mole of triethylamine (method B) [7].

Unsymmetrical Carbocyanines XII–XV. These compounds were obtained by condensation of 0.34 g (0.001 mole) of the ethiodide of VI or VII with an equimolar amount of the ethiodide of 2-β-acetanilidovinylbenzothiazole or -quinoline in 3–6 ml of acetic anhydride at 120–125° (for 10–15 min) in the presence of triethylamine. For the isolation of the carbocyanines, ether was added to the cooled reaction mixture, the resulting precipitate or resinous mass dissolved by heating in ethanol, and an equal volume of 10% potassium iodide solution was added to the solution.

Dimethylidynemerocyanines XVI–XVII. These compounds were synthesized by condensation of 0.34 g (0.001 mole) of the ethiodide of VI or VII with 0.30 g (0.001 mole) of 3-ethyl-5-acetanilidomethylenerhodanine in 5 ml of anhydrous ethanol in the presence of triethylamine by heating on the boiling-water bath (for 60 min).

Styryl Dyes XVII–XIX. These dyes were obtained by condensation of 0.34 g (0.001 mole) of the ethiodide of VI or VII with 0.17 g (0.001 mole) of p-dimethylaminobenzaldehyde in 5 ml of pyridine in the presence of piperidine by heating on a boiling-water bath (for 30 min).

All of the dyes were purified by crystallization from ethanol.

LITERATURE CITED

1. V. G. Zhiryakov and P. I. Abramenko, Sbornik Nauchn. Trudov Gosniikhimfotoproekt, No. 7, 62 (1972).
2. V. G. Zhiryakov and P. I. Abramenko, Khim. Geterotsikl. Soedin., No. 1, 166 (1967).
3. K. Fries, H. Heering, and E. Hemmecke, and G. Siebert, Ann., 527, 83 (1937).
4. Z. I. Moskalenko and M. A. Al'perovich, Khim. Geterotsikl. Soedin., No. 4, 626 (1967).
5. L. M. Sharkova, N. F. Kucherova, and V. A. Zagorevskii, Khim. Geterotsikl. Soedin., No. 8, 1075 (1972).
6. A. Dormal and J. Liebeer, Sci. Ind. Phot., 20, 451 (1949).
7. N. N. Sveshnikov and N. S. Stokovskaya, Zh. Vses. Khim. O-va, No. 7, 111 (1962).
8. F. M. Hamer, The Cyanine Dyes and Related Compounds, Wiley, New York-London (1964).
9. N. I. Fisher and F. M. Hamer, Proc. Roy. Soc. (London), 154A, 703 (1936).
10. P. I. Abramenko and V. G. Zhiryakov, Khim. Geterotsikl. Soedin., No. 12, 1611 (1972).
11. P. I. Abramenko and V. G. Zhiryakov, Khim. Geterotsikl. Soedin., No. 2, 227 (1965).

PYRIMIDINE-PYRIMIDYLIDENE TAUTOMERISM OF SOME 4-PYRIMIDYLMALONIC

ACID DERIVATIVES*

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2,6-Diphenyl-4-pyrimidylmalonic esters (I, II) 2,6-diphenyl-4-cyanoacetic ester (III), and 2,6-diphenyl-4-pyrimidylmalononitrile (IV) were obtained for the study of pyrimidine-pyrimidylidene tautomerism by condensation of 4-chloro-2,6-diphenylpyrimidine with the appropriate malonic acid derivatives. The structures of the tautomeric forms and the positions of the equilibria were studied by PMR, IR, and UV spectroscopic methods.

During a study of the structures of some 2-pyrimidylmalonic acid derivatives [1] it was established that in solution the latter exist either in the pyrimidine form or in the pyrimidylidene form. One should probably also expect instances of equilibria between two forms among compounds of this sort, i.e., tautomerism of the type



which is well known for sym-triazine derivatives [2] and some other nitrogen-containing heterocycles [3]. To obtain a pyrimidine-pyrimidylidene system with comparable amounts of both forms and to study the factors that affect their equilibrium, we synthesized 2,6-diphenyl-4-pyrimidylmalonic esters (I, II), 2,6-diphenyl-4-pyrimidylcyanoacetic esters (III), and 2,6-diphenyl-4-pyrimidylmalononitrile (IV).

The structures of the products were studied by means of PMR, IR, UV spectroscopy. The UV spectra of I-IV contain absorption maxima at $\lambda > 300$ nm, which cannot belong to tautomer A (see Fig. 1 and the scheme below) and indicate the presence of pyrimidylidene forms (B, C,

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