SYNTHESIS AND SPECTRAL CHARACTERISTICS OF PHOTOCHROMIC 5'-ARYL-1',3',3'-TRIMETHYL-6-NITRO-2H-CHROMENE-2-SPIRO-2'-INDOLINES

M. A. Gal'bershtam, N. M. Przhiyalgovskaya,
I. B. Lazarenko, V. S. Kononova,
and N. N. Suvorov

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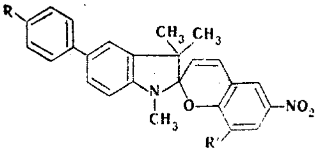
A number of photochromic indolinespirochromenes containing a phenyl or p-methoxyphenyl substituent in the 5' position of the indoline portion of the molecule were synthesized. The introduction of an aryl substituent in the 5' position gives rise to a slight bathochromic shift of the longwave absorption band of the merocyanine form of the spirochromene.

The investigation of the relationship between the structure of indoline spirochromenes and their photochromic properties creates the necessary prerequisites for the purposeful exploitation of photochromic materials with the required parameters. In order to study the effect of the introduction of aryl substituents in the indoline portion of the molecule on the spectral characteristics of the colored form of photochromic indolinespirochromenes, we synthesized a number of compounds containing a phenyl or p-methoxyphenyl substituent in the 5' position of the general formula



I-VI

I R=H, R'=OCH_3; II R=R'=H; III R=H, R'=Br; IV R=R'=OCH_3;
V R=OCH_3, R'=H; VI R=OCH_3, R'=Br

Compounds I and II are known [1, 2]. They were obtained by condensation of 5-phenyl-1,3,3-trimethyl 2-methyleneindoline with the corresponding salicylaldehydes. We used a similar method to synthesize III-VI.

All of the spirochromenes that we obtained in this study have photochromic properties at room temperature: on irradiation with UV light, colorless solutions in toluene and dioxane take on a blue-azure coloration, which gradually vanishes after irradiation is discontinued. The red-violet (spirochromenes II, III, V, and VI) or blue-violet (spirochromenes I and IV) alcohol solutions sustain an increase in their color intensity under the influence of UV irradiation.

Using the method in [3, 4] we determined the parameters of the absorption spectra of the merocyanine forms of spirans I-VI. The results are presented in Table 1, in which data for 1',3',3'-trimethyl-6-nitro-8-methoxy-2H-chromene-2-spiro-2'-indoline (VII), 1',3',3'-trimethyl-6-nitro-2H-chromene-2-spiro-2'-indoline (VIII) and 1',3',3'-trimethyl-6-nitro-8-bromo-2H-chromene-2-spiro-2'-indoline (IX), which we previously obtained in [3, 5, 6], are also presented for comparison.

The negative solvatochromism typical for merocyanine dyes [7] is characteristic for the primary absorption band of the colored form of all of the investigated spirochromenes: This band is shifted hypsochromically by 10-20 mm on passing from toluene to dioxane, whereas the shift is 50-70 nm on passing from toluene to alcohol, and the degree of solvatochromism increases only slightly in the order $OCH_3 < H < Br$ when the substit-

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TABLE 1. Characteristics of the Electronic Absorption Spectra of the Merocyanine Forms of Spirochromenes

Compound	Solvent	I band			II band		
		λ_{max}, nm	ε_{max}	f	λ_{max}, nm	ε_{max}	f
I	Toluene	609[a]	50000	0,76	401	26800	0,52
	Dioxane	600	58800	0,81	397	37100	0,66
	Alcohol	557[b]	26500	0,42	398	20200	0,39
II	Toluene	592[c]	47300	0,59	384	26000	0,37
	Dioxane	577	71000	0,88	377	41400	0,64
	Alcohol	534[d]	26700	0,41	388	11600	0,13
III	Toluene	598	27000	0,30	386	13900	0,27
	Dioxane	580	27700	0,35	385	15600	0,27
	Alcohol	531	22800	0,36	381	17700	0,36
IV	Toluene	612	33600	0,48	403	28700	0,54
	Dioxane	601	42500	0,58	401	23700	0,43
	Alcohol	563	30300	0,45	408	19200	0,30
V	Toluene	597	52900	0,62	382	23300	0,38
	Dioxane	583	68600	0,77	388	25000	0,34
	Alcohol	537	28900	0,42	376	17000	0,21
VI	Toluene	597	26500	0,30	387	15300	0,30
	Dioxane	582	37500	0,44	388	20600	0,34
	Alcohol	530	21500	0,35	387	17300	0,48
VII[6]	Toluene	598	—	—	—	—	—
VIII[5]	Toluene	596	53000	0,75	373	20000	0,34
	Dioxane	582	49000	0,61	375	27000	0,55
	Alcohol	523	26000	0,42	358	17000	0.45
IX	Toluene	591[6] 593[3]	— 49600	— 0,78	— 383	— 26800	— 0,38

[a] λ_{max} 606 nm[2], [b] λ_{max} 568 nm[2], [c] λ_{max} 606 nm[2], [d] λ_{max} 523 nm[2].

TABLE 2. Properties of the Compounds Obtained

Compound	mp, °C	UV spectrum in ethanol, λ_{max}, nm (log ε)	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
I	186—187[a, b]	285 (25100)	—	—	—	—	—	—	—	—
II	201—202[c, d]	247 (30000)	—	—	—	—	—	—	—	—
III	213—215	278 (18200)	$C_{25}H_{21}BrN_2O_3$	62,7	4,3	6,4	62,9	4,4	5,9	—
IV	199—201[e]	283 (28100)	$C_{27}H_{26}N_2O_5$	70,8	5,7	6,2	70,7	5,7	6,1	12
V	199—200[e]	276 (42500)	$C_{26}H_{24}N_2O_4$	72,7	5,6	6,8	72,9	5,6	6,5	8
VI	255—259	278 (29300)	$C_{26}H_{23}BrN_2O_4$[f]	61,7	4,7	5,8	61,5	4,6	5,5	22
X	177—180[a]	—	$C_{13}H_{14}N_2O$	72,6	6,6	12,9	72,9	6,6	13.1	93
XI	267[g]	—	$C_{19}H_{22}INO_3$[h]	55,2	5,6	3,6	56,0	5,4	3,4	—
XII	123—124[a]	—	$C_{19}H_{21}NO$	81,1	8,0	4,9	81,7	7,6	5,0	83

[a] From alcohol.

[b] According to the data in [2], this compound has mp 192-193°.

[c] From ethyl acetate.

[d] According to the data in [1], this compound has mp 200°.

[e] From isopropyl alcohol.

[f] Found: Br 15.5%. Calculated: Br 15.8%.

[g] From water.

[h] Found: I 31.7%. Calculated: I 31.2%.

uent in the 8 position is varied. The introduction of a methoxy group in the 8 position gives rise to a bathochromic shift of 15-25 nm of both absorption bands. In the case of 8-methoxy- and 8-bromospirans, the introduction of a phenyl substituent in the 5' position gives rise to a somewhat larger bathochromic shift. The secondary absorption band of the colored form of the spirochromenes, which is located on the boundary of the visible and UV region, does not experience such regular solvatochromic shifts as the primary band.

EXPERIMENTAL METHOD

The measurement of the absorption spectra of solutions of the spirochromenes in the photochemical steady states, the calculation of the extinction coefficients of the colorless and colored forms of the spirochromenes at various wavelengths, and the approximation of the data by Gaussian curves with an M-220 computer were accomplished as described in [3, 4].

The 4-amino-4'-methoxydiphenyl necessary for the synthesis of spirochromenes IV-VI was obtained from 4-nitrodiphenyl by the following known transformations: Nitration to 4,4'-dinitrodiphenyl [8], partial reduction of the dinitro compound [9], diazotization of the resulting nitro amine and subsequent decomposition of the diazonium salt in the presence of dilute sulfuric acid, treatment of the 4-hydroxy-4-nitrodiphenyl with dimethyl sulfate in alkaline media [8], and reduction of the 4-methoxy-4'-nitrodiphenyl with hydrazine hydrate in isopropyl alcohol [10]. 4-Methoxy-4'-hydrazinodiphenyl (X) was synthesized by the method used to prepare 4-hydrazinodiphenyl [11]. 5-(p-Methoxyphenyl)-2,3,3-trimethylindolinine methodide (XI) was obtained by the method in [12]. The properties of the compounds obtained are presented in Table 2.

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RESEARCH IN THE DIPIPERIDYL SERIES

XIX.* SYNTHESIS OF 4-(4-PIPERIDYL)-1,2,5,6-TETRAHYDROPYRIDINE

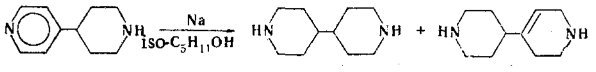
Yu. N. Forostyan and E. I. Forostyan

UDC 547.828:542.942.4:543.422.25.4.6'544

Hydrogenation of 4,4'-dipyridyl or 4-(4-piperidyl)pyridine with sodium in isoamyl alcohol gives a mixture of hydro derivatives, from which 4-(4-piperidyl)-1,2,5,6-tetrahydropyridine was isolated.

It has been shown that 4,4'-dipiperidyl (I) and 4-(4-piperidyl)pyridine (II) are formed in the hydrogenation of 4,4'-dipyridyl [2-4].

In a continuation of our earlier research [5] we have investigated the side products of the reaction and have shown that 4-(4-piperidyl)-1,2,5,6-tetrahydropyridine (III) is formed in 42% yield along with I in the hydrogenation of 4,4'-dipyridyl and II with sodium in isoamyl alcohol.



II I III

A one-proton broad signal with $\Delta\nu$ 1/2 Hz, which corresponds to an olefinic proton having spin–spin coupling constants on the order of 5-8 Hz from the protons of the methylene group, is observed in the NMR spectra of III at 2.3 ppm (in pyridine) and 5.4 ppm (in $CHCl_3$). This result unambiguously excludes from con-

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*See [1] for the preceding communication.

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