SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF SOME SPIROCHROMENES OBTAINED ON THE BASIS OF 4-AZAINDOLINE

D. P. Maisuradze, Sh. A. Akhobadze,
L. V. Devadze, and K. G. Dzhaparidze

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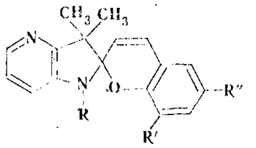
The condensation of N-methyl(ethyl)-3,3-dimethyl-2-methylene-4-azaindoline with salicylic acid derivatives was used to synthesize thermo- and photochromic spirochromenes. The kinetics of the spontaneous decolorization of these compounds in ethanol and toluene were studied. The photosensitivity to UV rays of the 4-azaindoline spirochromes is greater by a factor of 1.5 than that of the indoline analogs.

In indoline spirochromenes the indoline part of the molecule affects the spectral and kinetic characteristics of these compounds [1]. Spirochromenes in which the indoline part is replaced by an azaindoline ring are of undoubted interest in this connection.

Azaindole derivatives have higher solubilities in water, higher stabilities in both acidic and alkaline media, and increased basicities as compared with the indole analogs [2]. We therefore set out to synthesize various azaindoline spirochromenes. The synthesis and some properties of 7-azaindoline spirochromenes were described in [3]. The present paper is devoted to a description of spirochromenes synthesized on the basis of 4-azaindoline.

2,3,3-Trimethyl-4-azaindoline was synthesized from 3-aminopyridine [4], whereas the corresponding quaternary salts were obtained by heating the base indicated above with alkyl iodides. The spirochromenes were obtained by condensation of the quaternary salts in the presence of pyridine and piperidine or by the reaction of 2-methylene bases with the same aldehydes [5]. We used this method to obtain spirochromenes Ia-i.



I a-i

I a $R=CH_3$, $R'=H$, $R''=NO_2$; b $R=C_2H_5$, $R'=H$, $R''=NO_2$; c $R=CH_3$, $R'=OCH_3$, $R''=NO_2$; d $R=C_2H_5$, $R'=OCH_3$, $R''=NO_2$; e $R=CH_3$, $R'=Br$, $R''=NO_2$; f $R=C_2B_5$, $R'=Br$, $R''=NO_2$; g $R=CH_3$, $R'=NO_2$, $R''=Cl$; h $R=C_2H_5$, $R'=NO_2$, $R''=Cl$; i $R=C_2H_5$, $R'=R''=NO_2$

The compounds obtained are quite soluble in polar and nonpolar solvents [some of them (for example, Ic, and Id) dissolve in water up to a concentration of 10^{-5} mole/liter]. The thermodynamic equilibrium in solutions is shifted almost completely to favor the closed form (except for Ii).

The results of elementary analysis and the spectral and optical characteristics are presented in Table 1.

A comparison of the electronic absorption spectra of 4-azaindoline and indoline spirochromenes in the UV and visible regions shows that the spectra basically coincide. The slight bathochromic shift of the long-wave absorption band in the visible region (Table 1) is due to the increased electron-acceptor character of the pyridine ring as compared with the benzene ring.

A study of the kinetics of dark decolorization of solutions of 4-azaindoline spirochro-

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TABLE 1. Characteristics of the Synthesized Spirochromenes

Compound	λ_{max}, nm		$K_{BA} \cdot 10^3$ sec^{-1}		E_{BA}, kJ/mole		$\varepsilon^* \cdot 10^{-4}$, liters/mole·cm		Found, %			Empirical formula	Calc., %		
	ethanol	toluene	ethanol	toluene	ethanol	toluene	ethanol	toluene	C	H	Hal		C	H	Hal
Ia	549	610	3,20	8,60	89,0	84,0	4,0	4,3	66,7	5,0	—	$C_{18}H_{17}N_3O_3$	66,9	5,3	—
Ib	552	610	8,80	6,40	89,8	85,2	—	—	67,7	6,1	—	$C_{19}H_{19}N_3O_3$	67,6	5,6	—
Ic	565	606	15,00	15,00	76,9	100,3	3,0	3,2	64,6	5,5	—	$C_{19}H_{19}N_3O_4$	64,6	5,4	—
Id	565	606	15,00	11,00	100,3	100,3	—	—	65,0	5,7	—	$C_{20}H_{21}N_3O_4$	65,4	5,7	—
Ie	540	610	0,17	14,00	94,9	60,6	—	2,8	53,2	3,9	20,1	$C_{18}H_{16}BrN_3O_3$	53,7	4,0	19,9
If	549	610	0,22	7,00	94,9	60,6	—	—	55,3	4,9	19,1	$C_{19}H_{18}BrN_3O_3$	54,8	4,3	19,2
Ig	578	645	0,95	19,00	102,8	55,2	—	—	59,9	4,5	9,7	$C_{18}H_{16}ClN_3O_3$	60,4	4,5	9,9
Ih	581	645	0,95	17,00	102,8	55,2	—	—	61,5	4,9	10,14	$C_{19}H_{18}ClN_3O_3$	61,4	4,8	9,5
Ii	529	595	—	0,45	—	94,0	2,8	—	59,4	4,9	—	$C_{19}H_{18}N_4O_5$	59,7	4,7	—

*The coefficients of molar extinction were determined by the method described in [6].

menes showed that, as in the case of the indoline analogs [1], the process is described by two parallel first-order reactions; this is evidently due to the formation of different isomers or associates of the colored form. The rate constant of the fast process is an order of magnitude higher than the rate of the slow process. The rate of decolorization of 4-azaindoline spirochromenes, like that of the indoline spirochromenes, depends on the orientation and electronic properties of the substituents [7].

Replacement of the benzene ring by a pyridine ring gives rise to an increase in the light sensitivity by a factor of 1.5; this is explained basically by the difference in the quantum yields of decolorization of the colored form in the UV region (for example, for the nitro derivatives of the spirochromenes when λ = 366 nm, ϕ_{indole} = 0.1, and $\phi_{azaindole}$ = 0.01) [8].

EXPERIMENTAL

The spectral study of the synthesized compounds in the colorless and colored states was made with a Specord UV-vis spectrophotometer (c = $5 \cdot 10^{-5}$ mole/liter) at 10°C.

6-Nitro-2H-chromene-2-spiro-2'-1',3',3'-trimethyl-4'-azaindoline (Ia). A 1-g (3 mmole) sample of 2,3,3-trimethyl-4-azaindoline was dissolved in 25 ml of a mixture of ethanol with water (3:2), and an equimolar amount of 5-nitrosilicylaldehyde was added. The solution was red. The color became deeper when three drops of piperidine were added. The mixture was refluxed for 40 min. After a few hours, the precipitated light-yellow crystals were recrystallized from alcohol—water (3:1) to give a product with mp 158-158.5°C in quantitative yield.

6-Nitro-2H-chromene-2-spiro-2'-1'-ethyl-3',3'-dimethyl-4'-azaindoline (Ib). A 1-g (3 mmole) sample of 2,3,3-trimethyl-4-azaindoline was treated with a 17% solution of KOH at 40°C. This resulted in the formation of an oily liquid with a characteristic odor, for the extraction of which 50 ml of ether was added. The ether was removed by distillation on a water bath, and the residual crude oil was dissolved in 20 ml of ethanol, and an equimolar amount of 5-nitrosalicylaldehyde was added. The solution was red. The mixture was refluxed for 30 min. Pink-colored crystals (95%) formed after several days. Recrystallization gave light-yellow crystals with mp 118-119°C.

6-Nitro-8-methoxy-2H-chromene-2-spiro-2'-1',3',3'-trimethyl-4'-azaindoline (Ic). A 1-g (3 mmole) sample of 2,3,3-trimethyl-4-azaindoline was dissolved in 15 ml of pyridine, the solution was mixed with a hot solution of 0.65 g (3 mmole) of the corresponding aldehyde in the same amount of pyridine, and several drops of piperidine were added. The mixture was heated for 15 min, the solution was diluted with water, and the substance was extracted with benzene. After evaporation of the benzene at room temperature, the residue was dissolved in octane, and the solution was allowed to stand for crystallization. Light-yellow crystals with mp 173-174°C were isolated. The yield was 80%.

6-Nitro-8-methoxy-2H-chromene-2-spiro-2'-1'-ethyl-3',3'-dimethyl-4'-azaindoline (Id). A 1-g (3 mmole) sample of 2,3,3-trimethyl-4-azaindoline ethiodide was treated in the same way as Ib with the addition of an equimolar amount of the corresponding aldehyde. Recrystallization from octane gave light-yellow crystals with mp 131-132°C. The yield was 75%.

6-Nitro-8-bromo-2H-chromene-2-spiro-2'-1',3',3'-trimethyl-4'-azaindoline (Ie). This compound was obtained by dissolving 1 g (3 mmole) 2,3,3-trimethyl-4-azaindoline in 20 ml of a mixture of ethanol with water (1:1) and by the addition of a hot solution of 0.81 g (3 mmole) of the corresponding aldehyde in 15 ml of ethanol and two drops of piperidine. The solution was refluxed for 15 min, after which it was allowed to stand at room temperature for 2 days. Pink-colored crystals with mp 120°C (after recrystallization from octane) precipitated. The yield was quantitative.

6-Nitro-8-bromo-2H-chromene-2-spiro-2'-1'-ethyl-3',3'-dimethyl-4'-azaindoline (If). This compound was obtained by the addition of 0.78 g (3 mmole) of the corresponding aldehyde to 1 g (3 mmole) of 2,3,3-trimethyl-4-azaindoline methiodide. Recrystallization from octane gave grayish-pink crystals with mp 143.5-144°C. The yield was 85%.

8-Nitro-6-chloro-2H-chromene-2-spiro-2'-1',3',3'-trimethyl-4'-azaindoline (Ig). A 1-g (3 mmole) sample of 2,3,3-trimethyl-4-azaindoline was dissolved in a small amount of pyridine, and a few drops of piperidine and a hot solution of 0.67 g (3 mmole) of the corresponding aldehyde in pyridine were added. The solution was evaporated at room temperature, and the residue was refluxed with octane. The solution was filtered and allowed to stand for crystallization. Yellow crystals with mp 147-147.5°C were obtained. The yield was 70%.

8-Nitro-6-chloro-2H-chromene-2-spiro-2'-1'-ethyl-3',3'-dimethyl-4'-azaindoline (Ih). 1-g (3 mmole) sample of 2,3,3-trimethyl-4-azaindoline was treated in the same way as Ib, and an equimolar amount of the corresponding aldehyde was added. The solution was green, and the color became deeper when the solution was heated. Recrystallization of the product from octane gave yellow crystals with mp 146-146.5°C. The yield was 90%.

6,8-Dinitro-2H-chromene-2-spiro-2'-1'-ethyl-3',3'-dimethyl-4'-azaindoline (Ii). A 1-g (3 mmole) sample of 2,3,3-trimethyl-4-azaindoline was treated in the same way as in the preceding experiment, and an equimolar amount of the corresponding aldehyde was added. The solution was purple-red. Dark-red crystals with a metallic luster and a green tint precipitated when the solution was heated. Recrystallization of the precipitate gave a product with mp 231-232°C. The yield was almost quantitative.

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