

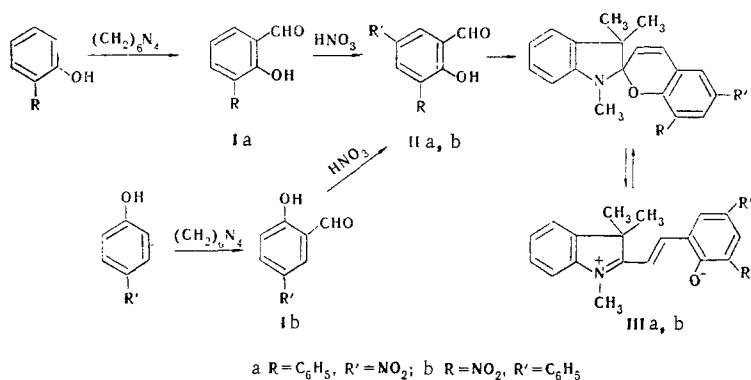
SYNTHESIS AND SPECTRAL CHARACTERISTICS  
OF PHOTOCHEMIC 6- AND 8-PHENYL- SUBSTITUTED  
INDOLINE SPIROCHROMENES

E. V. Braude and M. A. Gal'bershtam

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Two photochromic indoline spirochromenes were synthesized. The introduction of a phenyl group into the 6 or 8 position causes a bathochromic shift of the bands in the electronic absorption spectrum of the merocyanine form.

In a search for structural factors that affect the spectral characteristics of the colored form of spirochromenes [1], we obtained the corresponding spirans (III) containing a phenyl substituent in the pyran portion of the molecule from 3-phenyl-5-nitro- (IIa) and 5-phenyl-3-nitrosalicylaldehyde (IIb) [2] by reaction with 1,3,3-trimethyl-2-methyleneindoline:



We were able to obtain 3-phenylsalicylaldehyde (Ia), which was previously synthesized by the Gattermann reaction [3], by the Duff method by reaction in glacial acetic acid, despite the data of Ligett and Diehl [4] indicating that o-hydroxyphenyl does not undergo this reaction.

Spirans IIIa, b have photochromic properties at room temperature: colorless solutions of them in toluene and dioxane take on a blue-azure coloration on irradiation with UV light that gradually disappears after irradiation is discontinued. Violet-colored alcohol solutions of the spiroan sustain an increase in the intensity of the coloration under the influence of UV irradiation and are decolorized on irradiation with an incandescent lamp.

We used the method in [5] to determine the parameters of the absorption spectra of the merocyanine forms of spirans IIIa, b and also, for comparison of 1',3',3'-trimethyl-6-nitro-2H-chromene-2-spiro-2'-indoline (IIIc,  $R = H$ ,  $R' = NO_2$ ) and 1',3',3'-trimethyl-8-nitro-2H-chromene-2-spiro-2'-indoline (IIId,  $R = NO_2$ ,  $R' = H$ ) (Table 1). The introduction of a phenyl group into the 6 or 8 position leads to a bathochromic shift of all of the absorption bands of the merocyanine form, which may reach 30 nm for the first band and 15-20 nm for the second band; the oscillator force of the bands apparently does not change substantially.

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

Compound	Solvent	I band			II band		
		$\lambda_{max}$ , nm	$\epsilon_{max}$	$f$	$\lambda_{max}$ , nm	$\epsilon_{max}$	$f$
IIIa	Alcohol	554	40000	0,60	379	26000	0,59
	Dioxane	592	53000	0,67	389	32000	0,59
	Toluene	602	46000	0,65	389	29000	0,48
IIIb	Alcohol	578	21000	0,31	368	10000	0,29
	Dioxane	622	41000	0,53	388	25000	0,41
	Toluene	631	33000	0,47	393	19000	0,36
IIIc	Alcohol	523 (532 <sup>b</sup> )	26000	0,42	358	17000	0,45
	Dioxane	582	49000	0,61	375	27000	0,55
	Toluene	596 (598 <sup>b</sup> )	53000	0,75	373	20000	0,34
IIId	Alcohol	542 (544 <sup>b</sup> )	34000	0,48	358	10000	0,31
	Dioxane	596	70000	0,94	383	34000	0,47
	Toluene	598 (602 <sup>b</sup> )	98000	1,26	389	29000	0,35

A bathochromic shift is also observed on passing from 6-nitro-substituted compounds to 8-nitro-substituted compounds. The negative solvatochromism characteristic for most merocyanine forms of spiropyrans [5] is observed for IIIa-d.

## EXPERIMENTAL

The measurement of the absorption spectra of the starting solutions of the spirochromenes in the photosteady state, the calculation of the extinction coefficients of the colorless and colored forms of the spirochromenes at various wavelengths, and the approximation of the data obtained by means of Gaussian curves with an M-220 computer were realized as described in [5]. The IR spectra of KBr pellets were measured with a UR-20 spectrometer. Analysis of gas-liquid chromatography (GLC) was realized with an LKhM-7A chromatograph with a 2-m long column filled with Chromosorb W impregnated with SE-30 silicone rubber (5%). The column temperature was 200°, the carrier gas was helium, and the detector was a katharometer.

3-Phenylsalicylaldehyde (Ia). Glacial acetic acid (200 ml) and 490 g (3.5 mole) of urotropin were added to 70 g (0.41 mole) of o-hydroxydiphenyl, and the mixture was heated for 7 h on a boiling-water bath. It was then diluted with a hot mixture of 0.5 liter of water and 0.5 liter of concentrated HCl. The mixture was then stirred for 1 h, cooled, and allowed to stand overnight. The resulting precipitate was removed by filtration, and the filtrate was then distilled. The distillate was extracted with chloroform, and the extract was dried with magnesium sulfate. The solvent was removed by distillation, and the residue was vacuum distilled to give a mixture of o-hydroxydiphenyl and aldehyde Ia (3:2 according to GLC data) with bp 140–143° (10 mm). This fraction was separated by means of preparative GLC with a Khrom-31 chromatograph [with a 5-m long column filled with Chromaton H impregnated with Apiezon L (15%) at 275°] to give 4.08 g (5%) of aldehyde Ia with mp 68–69° (mp 69–71.5° [3]). IR spectrum: 1650  $\text{cm}^{-1}$  (C=O).

5-Phenylsalicylaldehyde (Ib). A mixture of 500 g of glycerol and 70 g of boric acid was heated at 170° for 2 h with removal of the water by distillation. The mixture was then heated at the same temperature in *vacuo* (at 20 mm) until water evolution ceased completely, after which 50 g (0.36 mole) of urotropin and 50 g (0.29 mole) of p-hydroxydiphenyl were added. At the end of the exothermic reaction, the mixture was heated at 160° for 1 h. It was then cooled to 100°, 260 ml of 30% sulfuric acid was added, and the mixture was steam distilled. The distillate was extracted with ether, and the extract was dried with magnesium sulfate. The solvent was removed by vacuum distillation to give 3.49 g (6%) of aldehyde Ib with bp 157–165° (0.01 mm) and mp 107° (mp 102° [7]). IR spectrum: 1650  $\text{cm}^{-1}$  (C=O).

5-Nitro-3-phenylsalicylaldehyde (IIa). A solution of 0.3 ml (7 mmole) of fuming nitric acid (sp. gr. 1.51) in 10 ml of acetic acid was added in the course of 30 min at 10–15° to a mixture of 0.8 g (4 mmole) of Ia and 30 ml of glacial acetic acid, after which the mixture was stirred for 2 h and poured over a mixture of 50 g of ice and 30 ml of water. The resulting yellow precipitate was removed by filtration and washed with water to give 0.67 g (68%) of aldehyde IIa with mp 139–140°. Two recrystallizations from alcohol gave 0.3 g (31%) of aldehyde IIa [2] with mp 144–145°. IR spectrum: 1640  $\text{cm}^{-1}$  (C=O).

3-Nitro-5-phenylsalicylaldehyde (IIb). This compound, with mp 115-116°, was obtained as described above in 30% yield from aldehyde IIb. IR spectrum: 1660  $\text{cm}^{-1}$  (C=O) [2].

1',3',3'-Trimethyl-6-nitro-8-phenyl-2H-chromene-2-spiro-2'-indoline (IIIa). A solution of 0.4 g (2.3 mmole) of freshly distilled 1,3,3-trimethyl-2-methyleneindoline in 10 ml of alcohol was added in the course of 30 min to a solution of 0.47 g (2 mmole) of aldehyde IIa in 50 ml of ethanol, and the mixture was refluxed for 2 h. The resulting precipitate was separated and crystallized from alcohol containing activated charcoal. The hot alcohol solution was filtered through a 1-cm thick layer of bentonite, after which the product was crystallized from hexane to give 145 mg (19%) of spirochromene IIIa as a light-yellow powder with mp 166-167°. UV spectrum in octane,  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 206 (42,000), 243 (44,000), and 315 (15,000). Found: C 75.2; H 5.4; N 7.1%.  $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_3$ . Calculated: C 75.4; H 5.6; N 7.0%.

1',3',3'-Trimethyl-6-phenyl-8-nitro-2H-chromene-2-spiro-2'-indoline (IIIb). This compound, with mp 152-153° (from alcohol), was similarly obtained in 15% yield from aldehyde IIb. UV spectrum in octane,  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 207 (27,000) and 248 (30,000). Found: C 74.9; H 5.6; N 7.2%.  $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}_3$ . Calculated: C 75.4; H 5.6; N 7.0%.

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