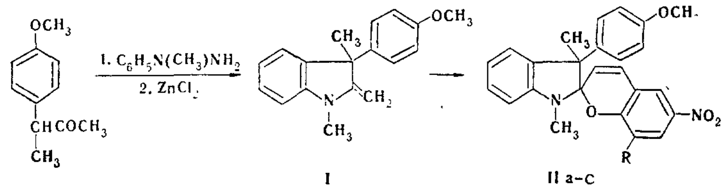
SYNTHESIS OF 3-(p-METHOXYPHENYL)-1,3-DIMETHYLSPIRO(INDOLINE-2,2'-[2H-1]-BENZOPYRANS) AND INVESTIGATION OF THE ELECTRONIC ABSORPTION SPECTRA OF THEIR MEROCYANINE FORMS

M. A. Gal'bershtam and N. P. Samoilova

UDC 541.145:547.752'814.1.07:543.422.6

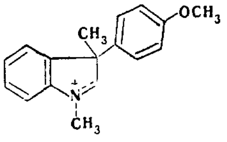
Photochromic indoline spiropyrans containing a p-methoxyphenyl substituent in the 3-position were synthesized, and the electronic absorption spectra of their merocyanine forms were measured.

In order to study the effect of substituents on the photochromic properties of 1,3-dimethyl-3-aryl-substituted indoline spiropyrans [1] we synthesized some 3-(p-methoxyphenyl)-1,3-dimethylspiro(indoline-2,2'-[2H-1]benzopyrans) (IIa-c) from 1,3-dimethyl-3-(p-methoxyphenyl)-2-methyleneindoline I, which was obtained by the Fischer reaction from 3-(p-methoxyphenyl)-2-butanol [2] and α-methylphenylhydrazine. Compound I was subjected, without isolation, to reaction with the appropriate nitrosalicylaldehydes.



II a R=H; b R=Br; c R=OCH₃

Molecular peaks with m/e 414 and 444, respectively, are observed in the mass spectra of spiropyrans IIa, c. Two molecular peaks at m/e 494 and 492, which correspond to molecules containing ^{81}Br and ^{79}Br isotopes, are characteristic for spiropyran IIb, which contains a bromine atom. Peaks of fragments formed by splitting out of one, two, and three methyl groups from the molecular ion are also observed in the spectra. The most intense peak in the mass spectra of the investigated spiropyrans is the peak with m/e 251, which corresponds to the indoline fragment



m/e 251

Spiropyrans IIa-c have photochromic properties at room temperature: colorless solutions in toluene and dioxane take on a blue-azure color on irradiation with UV light that gradually disappears after irradiation is discontinued. Alcohol solutions of spiropyrans IIa-c are red-violet, and the intensity of their coloration increases during UV irradiation and decreases on irradiation with the total light of an incandescent lamp.

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1041-1043, August, 1974. Original article submitted August 21, 1973.

TABLE 1. Absorption Spectra of the Merocyanine Forms of Spiropyrans IIa-c

Compound	Solvent	I band			II band		
		λ_{max},mm	ε_{max}	f	λ_{max},mm	ε_{max}	f
IIa	Alcohol	537	32000	0,43	363	15000	0,38
IIa	Dioxane	585	36000	0,45	367	17000	0,33
IIa	Toluene	587	71000	0,83	374	31000	0,47
IIb	Alcohol	551	30000	0,41	370	21000	0,52
IIb	Dioxane	584	36000	0,49	375	19000	0,34
IIb	Toluene	591	46000	0,55	379	25000	0,40
IIc	Alcohol	552	21000	0,35	—*	—	—
IIc	Dioxane	595	55000	0,83	397	38000	0,61
IIc	Toluene	597	67000	0,67	399	27000	0,46

---

*This band could not be measured because of the low sensitivity of the solution to the effect of irradiation in the UV and visible region.

From the spectral data (Table 1) it can be concluded that the electronic absorption spectra of the colored forms of the spiropyrans are subject to the regularities characteristic for merocyanine dyes. They contain two nonoverlapped symmetrical bands at 320-700 nm. On passing from alcohol to dioxane and toluene their maximum are shifted bathochromically by 30-50 nm for the band at 540 nm and by 4-10 nm for the maximum at 360-370 nm. Thus, negative solvatochromism is characteristic for the colored forms of the spiropyrans obtained in this study [4]. As in the case of 3-phenyl-substituted compounds [1], replacement of the hydrogen atom in the 8'-position by a bromine atom or a methoxy group for spiropyrans IIa-c leads to an appreciable bathochromic shift of both bands. A comparison of the data obtained in this study with the λ_{max} values for 1,3,3-trimethyl-6'-nitrospiro(indoline-2,2'-[2H-1]benzopyran) and also with the values for 3-phenyl-substituted compounds [1] makes it possible to conclude that replacement of a methyl group by an aryl group does not lead to a substantial change in the spectra of the photocolored forms. The position of the abosrption bands does not change in dioxane, a bathochromic shift is observed in alcohol, while a hypsochromic shift is observed in toluene; the shift in the bands on passing from alcohol to toluene for 3-aryl-substituted compounds is somewhat less than in the case of 3-methyl-substituted spiropyrans.

Thus, modification of the properties of the spiropyrans by introduction of the necessary substituents into the 3-position is possible without a substantial change in the spectral characteristics of the photocolored forms.

EXPERIMENTAL

The measurement of the absorption spectra of solutions of the spiropyrans, calculation of the extinction coefficient of the colorless and colored forms at various wavelengths, and approximation of the data obtained by means of Gaussian curves with an M-220 computer were carried out as described in [3]. The mass spectra were measured with a MATCH-6 spectrometer at an ionization potential of 70 eV.

1,3-Dimethyl-3-(p-methoxyphenyl)-2-methyleneindoline (I). A mixture of 17.8 g (0.1 mole) of 3-(p-methoxyphenyl)-2-butanone [2] and 12.2 g (0.1 mole) of α-methylphenylhydrazine was heated on a boiling-water bath for 24 h, after which it was cooled, 123 ml of absolute ethanol and 135.3 g of fused zinc chloride were added, and the mixture was heated for another 1.5 h. It was then cooled and decomposed with 150 ml of 30% sodium hydroxide solution and extracted with ether. The extract was dried over potassium hydroxide, the ether was evaporated, and the residue was vacuum distilled to give 8 g (30%) of 1,3-dimethyl-3-(p-methoxyphenyl)-2-methyleneindoline as a yellow oil with bp 150-160° (12 mm); the product was rapidly oxidized on storage.

Spiropyrans IIa-c. An 8-mmole sample of the approxpriate nitrosalicylaldehyde in 10 ml of ethanol was refluxed with 7.8 mmole of 1,3-dimethyl-3-(p-methoxyphenyl)-2-methyleneindoline for 2 h. The solid material was removed by filtration and crystallized from alcohol. Spiropyran IIa with mp 186-187° was obtained in 46% yield. Mass spectrum, m/e: 414, 399, 384, 369, and 251. Found: C 72.3; H 5.3; N 6.7%. $C_{25}H_{22}N_2O_4$. Calculated: C 72.4; H 5.3; N 6.7%. Compound IIb with mp 146-147° was obtained in 45% yield. Mass spectrum, m/e: 494, 492, 379, 377, 364, 362, 349, 347, and 251. Found: C 61.0; H 4.4; N 5.8%. $C_{25}H_{21}BrN_2O_4$. Calculated: C 60.8; H 4.3; N 5.7%. Compound IIc with mp 192-193° was obtained in 33% yield. Mass spectrum, m/e: 444, 429, 414, 399, and 251. Found: C 70.4; H 5.5; N 6.0%. $C_{26}H_{24}N_2O_5$. Calculated: C 70.3; H 5.4; N 6.3%.

LITERATURE CITED

1. M. A. Gal'bershtam and N. P. Samoilova, Khim. Geterotsikl. Soedin., 1209 (1973).
2. E. Okerberger and H. Gacner, J. Amer. Chem. Soc., 80, 4556 (1958).
3. M. A. Gal'bershtam, L. M. Mikheeva, and N. P. Samoĭlova, Khim. Geterotsikl. Soedin., 1534 (1972).
4. A. I. Kiprianov, Usp. Khim., 29, 1336 (1960).
5. E. V. Braude and M. A. Gal'bershtam, Khim. Geterotsikl. Soedin., 943 (1974).