EFFECT OF SUBSTITUENTS IN THE 5 AND 8' POSITIONS ON THE ABSORPTION SPECTRA OF MEROCYANINE FORMS OF SPIROPYRANS

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UDC 547.752'814.5'642:541.143:543.422.6

The absorption spectra in the visible region of the merocyanine forms of 1,3,3-trimethyl-6'-nitrospiro[indoline-2,2'-[2H-1]benzopyrans] with different substituents in the 5 and 8' positions were measured. The results are in agreement with concepts regarding the change in the contribution of the polar and nonpolar forms to the resulting merocyanine structure on introduction of substituents.

In the course of an investigation of the effect of substituents on the photochromic properties of indoline spiropyrans, we studied the relationship between the character of the substituents in the 5 and 8' positions of spiropyrans and the rate constants for the dark decolorization of their photocolored solutions [1]. It seemed of interest to study the effect of these same substituents on the spectral characteristics of the colored (merocyanine) forms of the spiropyrans. Using a previously developed method [2], we measured the absorption spectra of the photocolored forms of some spiropyrans with different substituents in the 5 and 8' positions. In view of the fact that the differences in the positions of the maxima of the absorption bands of the colored forms of spiropyrans are extremely insignificant, it was necessary to convince ourselves of the sufficient accuracy of the method used. For this, in the case of one of the spiropyrans, we

TABLE 1. Reproducibility of the D/D_{600} Values during Measurement of the Absorption Spectra of Photocolored Solutions of 1,3,3-Trimethyl-6'-nitro-8'-bromospiro[indoline-2,2'-[2H-1]benzopyran]

c, M λ, nm	D/D_{600}			
	$2{,}74 \cdot 10^{-5}$	$3{,}68 \cdot 10^{-5}$	$4{,}41 \cdot 10^{-5}$	$5{,}10 \cdot 10^{-5}$
490	0,040	0,071	0,060	0,063
500	0,110	0,117	0,123	0,116
510	0,181	0,185	0,169	0,186
520	0,285	0,260	0,239	0,257
530	0,363	0,352	0,341	0,350
540	0,490	0,507	0,494	0,495
550	0,662	0,609	0,645	0,634
560	0,753	0,784	0,762	0,756
570	0,841	0,864	0,837	0,865
580	0,904	0,954	0,947	0,929
590	0,890	0,962	0,942	1,001
600	1,000	1,000	1,000	1,000
610	0,912	0,962	0,981	0,987
620	0,929	0,955	0,945	0,892
630	0,963	0,942	0,895	0,914
640	0,952	0,912	0,862	0,845
650	0,391	0,314	0,391	0,361
660	0,226	0,228	0,272	0,257
670	0,171	0,160	0,183	0,153
680	0,083	0,129	0,129	0,122
690	0,045	0,089	0,090	0,076

All-Union Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 659-662, May, 1973. Original article submitted January 6, 1972.

studied the reproducibility of the results in four independent experiments that differed from one another with respect to the concentration of the starting solutions and the intensity of the activating UV spectrum. For convenience in the comparison, the optical densities obtained at various wavelengths were scaled to relative values D/D_{600}, where D is the optical density at the measured wavelength, and D_{600} is the optical density of the same solution at 600 nm. The results are presented in Table 1. As seen from Table 1, the scatter in the results at different wavelengths may reach 20%.

TABLE 2. Results of an Approximation of the Experimental Data Presented in Table 1

$c \cdot 10^5$, M	ν_{max}, cm^{-1}	λ_{max}, nm	δ, cm^{-1}
2,74	16915	591,17	1503
3,68	16915	591,17	1462
4,41	16910	591,39	1483
5,10	16928	590,74	1461
Average	16917	591,12	1477

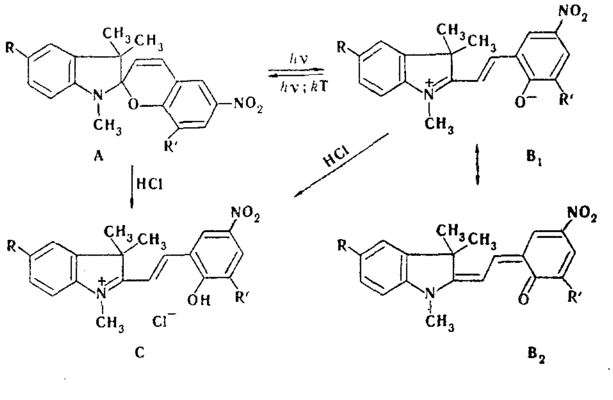
The results of an approximation of the experimental data by Gaussian curves are presented in Table 2, from which we obtain the position of the absorption maximum (ν_{max} in reciprocal centimeters or λ_{max} in nanometers) and the half-width of the band (δ in reciprocal centimeters). As seen from the data, the scatter in the λ_{max} values does not exceed 1 nm, while the scatter in the δ values does not exceed 50 cm^{-1} (~2 nm). Thus the accuracy in the method adopted can be considered to be completely adequate.

The λ_{max} values determined for a number of spiropyrans are presented in Table 3. These data are in good agreement with concepts regarding the change in the contribution of the polar and nonpolar forms to the resulting merocyanine structure on introduction of substituents [3, 4]. As seen from the data, the introduction of electron-donor substituents into the 8' position causes a bathochromic shift of the absorption band up to 6 nm; this corresponds to a decrease in the contribution of the polar structure. The introduction of electron-acceptor substituents into the 8' position produces almost no change in the position of the maximum. The absence of an appreciable hypsochromic shift in this case is apparently associated with the participation of the unshared pair of electrons of the halogen atom or of the π electrons of the C = O bond in the $COOCH_3$ and $COOC_2H_5$ substituents in the overall conjugation chain of the molecule, which causes a bathochromic shift in the absorption band. The introduction of an electron-donor substituent into the 5 position causes a hypsochromic shift of the absorption band; this attests to an increase in the contribution of the polar structure. However, the introduction of an electron-acceptor substituent into the 5 position causes a bathochromic shift; this corresponds to a decrease in the contribution of the polar structure.

It should be noted that the effect of substituents on the position of the maximum of the absorption band of the merocyanine form of spiropyran is manifested to an extremely insignificant degree because of the fact that the system, like an unusual buffer, reacts to the introduction of a substituent via several mechanisms, the effects of which are directed counter to one another. In the case where the system loses its capacity to react to the introduction of a substituent by redistribution of the contributions of the polar and nonpolar forms in the resulting molecular structure, this "buffer effect" should vanish. We confirmed this by measurement of the position of the maximum of the absorption band in the yellow salt-like compounds formed during the action of gaseous hydrogen chloride on solutions of the spiropyrans.

TABLE 3. Position of the Maxima of the Absorption Bands of the Merocyanine (B) and Salt (C) Forms of Spiropyrans

R	R'	λ_{max}, nm	
		B	C
H	OCH_3	598	379
H	CH_3	596	401
H	$CH_2CH{=}CH_2$	597	402
H	H	593	409
H	Br	591	391
H	$COOCH_3$	593	394
H	$COOC_2H_5$	593	395
CH_3	$COOC_2H_5$	591	400
F	$COOC_2H_5$	596	396
Cl	$COOC_2H_5$	596	398
Br	$COOC_2H_5$	595	399
CH_3	H	—	411
Cl	H	—	414
I	H	—	422
NO_2	H	—	412



The data are presented in Table 3. As seen from these data, the character of the effect of substituents on the position of the absorption band changes sharply, and the shifts of the maximum of the absorption band on introduction of a substituent into the 5 and 8' positions reach several tens of nanometers. A considerable hypsochromic shift is observed when a substituent of any type is introduced into the 8' position, while the introduction of a substituent into the 5 position causes an appreciable bathochromic shift in the case of both donor and acceptor substituents. Similar shifts of the absorption maxima are characteristic for cyanine dyes when substituents are introduced [5].

EXPERIMENTAL

To measure the absorption spectra of the merocyanine forms of the spiropyrans we selected several compounds that we had previously used in our kinetic investigations [1]. Toluene, purified by the method in [6], was used as the solvent. The measurement of the spectra of the starting solutions, the photocoloration reaction, the measurement of the transmission of the solutions in the photosteady state, the calculation of the experimental values of the optical density of the photocolored solutions at different wavelengths in the visible portion of the spectrum, and the approximation of the experimental data by Gaussian curves by means of an M-220 computer were accomplished as described in [2]. The essence of the method used consists in the following. The spectrum of the photocolored spiropyran solution cannot be measured with a normal spectrophotometer, since the solution changes during the measurement because of the dark reaction. In the method, the spectrum of the photocolored solutions was measured in the photosteady state under the activating beam. For this, we used a unit designed for kinetic measurements. The measurements were made repeatedly at different wavelengths, and the experimental dependence $D = f(\lambda)$ was constructed from the points. The experimental dependence obtained was approximated by a Gaussian curve for the accurate determination of the position of the maximum of the absorption band.

To measure the absorption spectra of the yellow salt-like compounds formed during the action of gaseous hydrogen chloride on the spiropyran solutions, we used dioxane, since the solubility of these compounds in toluene is extremely low. The dioxane was purified by the method in [7]. The spiropyran solution ($\sim 1 \cdot 10^{-4}$ M) was saturated with anhydrous gaseous hydrogen chloride at ~ 20° for 5 min, after which the spectrum of the solution was measured with a Unicam SP-800 spectrophotometer.

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