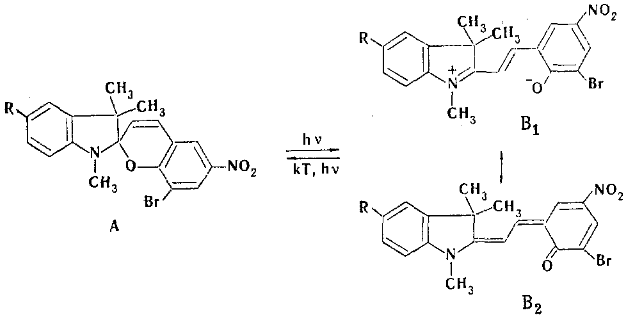
ELECTRONIC ABSORPTION SPECTRA OF MEROCYANINE FORMS OF SPIROPYRANS

M. A. Gal'bershtam, L. M. Mikheeva,
and N. P. Samoilova

UDC 547.754'814.1'642:541.143

A simple method is proposed for the measurement of the absorption spectra in the visible and UV regions of photocolored solutions of spiropyrans, formed by the action of constant low-intensity UV irradiation, and for the construction, on the basis of these data, of the absorption spectra of the merocyanine forms of spiropyrans. The absorption spectra of the merocyanine forms of two spiropyrans in various solvents are examined.

The photochromism of spiropyrans is due to the conversion, under the influence of activating UV irradiation, of the colorless spiropyran form (A) to the colored merocyanine form (B), the structure of which is intermediate between dipolar structure B_1 and nonpolar structure B_2 [1].



The electronic absorption spectrum of the merocyanine form is one of the most important characteristics that describe the photochromic behavior of spiropyrans. However, the determination of the true spectrum (including the UV region) and the extinction coefficients (ε) of the merocyanine form of spiropyrans presents considerable difficulties [1,2], which are associated with the impossibility of separating the merocyanine and spiropyran forms of spiropyrans, which exist in equilibrium. For this reason, various chemical [3,4] and indirect spectroscopic methods [1,2,5,6] have been proposed for the determination of the ε values.

The absorption spectra of solutions of spiropyrans containing a considerable amount of the merocyanine form can be measured only under the condition that the concentration of the merocyanine form does not change appreciably during the measurement. In this connection, measurements of this sort in photocolored solutions are made using a pulse technique [7,8] and also at low temperatures [9,10]; thermostatted solutions of spiropyrans in polar solvents [11,12] or solutions in nonpolar solvents with a very high starting concentration of spiropyran [13] are also used to measure the spectra. A special extremely complex apparatus that makes it possible to measure the spectra of a solution in the photosteady state [2] is used with activating radiation sources of constant action to measure the absorption spectra of photocolored solutions of spiropyrans in nonpolar solvents at room temperature.

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1534-1538, November, 1972. Original article submitted November 3, 1971.

In the course of our investigation of the photochromism of spiropyrans [14, 15], it became necessary to measure the absorption spectra of photocolored solutions formed by the action of low-power sources of UV radiation of constant action at room temperature. The pulse method, which uses the activating pulses of high-intensity UV light, could give a spectral pattern complicated by the presence of short-lived intermediate forms [7]. In this connection, we developed a method for the measurement of the spectra of photocolored solutions of spiropyrans by means of a simple apparatus used in kinetic studies.

The data obtained, in conjunction with the ε values measured by an independent method [4], made it possible to construct the absorption spectra of the merocyanine forms of spiropyrans.

In carrying out the kinetic studies, we used an apparatus that makes it possible, during the colorizing and dark decolorizing reactions, to measure the change in light transmission of the spiropyran solution at a fixed probe light wavelength in the absorption band of the merocyanine form of the spiropyran in the visible region of the spectrum. The optical density at this wavelength increased during the photocoloration reaction and reached a constant value in the photosteady state. Using low-intensity sources of activating UV radiation (which made it possible to disregard processes involving the photodestruction of the spiropyrans) and fresh portions of the starting solution for repeated measurements, we found that these values are reproducible from experiment to experiment with an accuracy of ± 5%. These results are evidence that the same photosteady state is reproduced from experiment to experiment, within the limits of the experimental errors. In this connection, it seemed possible, by changing the wavelength of the probe light from experiment to experiment, to construct the absorption spectrum of the spiropyran solution in the photosteady state from the points.

We will select the "reference" wavelength as that wavelength (λ_{ref}) in the absorption band of the merocyanine form of spiropyran in the visible region of the spectrum for which the extinction coefficient (ε_{ref}) is known [4]. We designate the optical densities of the photocolored and starting solution at wavelength λ_{ref} and at any fixed wavelength λ, respectively, as $D_{ref}^{(1)}$ and $D_{ref}^{(2)}$; $D^{(1)}$ and $D^{(2)}$; we will also introduce the following symbols: ε_A is the extinction coefficient of the colorless spiran form of the spiropyran at wavelength λ, C_0 is the molar concentration of the starting spiropyran solution, l is the layer thickness in the direction of the probe light (in centimeters), and ε_B is the extinction coefficient of the merocyanine form of the spiropyran at wavelength λ.

The following equations are valid when the system follows the Lambert–Beer Law:

$$\varepsilon_A = \frac{D^{(2)} - D^{(1)}K}{C_0 l (1-K)},$$

$$\varepsilon_B = \frac{\varepsilon_{ref} D^{(1)}}{D_{ref}^{(1)}} - \left(\frac{C_0 l \varepsilon_{ref}}{D_{ref}^{(1)}} - 1 \right) \varepsilon_A,$$

where

$$K = \frac{D_{ref}^{(2)}}{D_{ref}^{(1)}}.$$

Thus, by measuring the absorption spectrum of the starting solution (which generally may contain not only the colorless spiran form but also the colored merocyanine form), the absorption spectrum of the photocolored solution in the photosteady state, and the extinction coefficient of the merocyanine form of the spiropyran at the "reference" wavelength in the absorption band in the visible region, one can construct the absorption spectrum of the merocyanine form of the spiropyran [$\varepsilon_B = f(\lambda)$] as well as the absorption spectrum of the colorless spiran form [$\varepsilon_A = f(\lambda)$].

We studied the absorption spectra in the visible and UV regions of alcohol, dioxane, and toluene solutions of 1,3,3-trimethyl-6'-nitro-8'-bromospiro(indoline-2,2'-2H-chromene) (I, R = H) [11] and 1,3,3-trimethyl-5-fluoro-6'-nitro-8'-bromospiro(indoline-2,2'-2H-chromene) (II, R = F) [15] (see the scheme above). In the dark in concentrations on the order of 10^{-4} M, these spiropyrans form colorless solutions in toluene and dioxane and red-violet solutions in alcohol. In this connection, we measured the absorption spectra of the photocolored solutions in toluene and dioxane by means of a kinetic apparatus and the absorption spectra of alcohol solutions by means of an SFD-2 spectrophotometer.

It should be noted that the colored alcohol solutions of I and II, which contain an appreciable amount of the merocyanine form, are thermodynamically stable. We decolorized these solutions by irradiation with the full light of an incandescent lamp, after which we measured their absorption spectra in the UV region; in this case, the spectrum did not have time to change appreciably during the measurements.

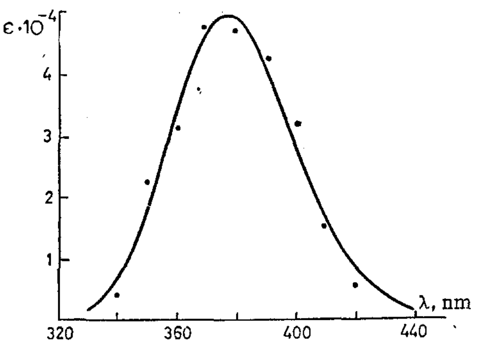


Fig. 1. Second absorption band of the merocyanine form of spiropyran II in dioxane.

According to the data in [2], several broad, almost symmetrical bands, which are enveloped by smooth curves without inflections and sharp peaks, are observed in the spectra of photocolored solutions of spiropyrans in dioxane. There are also broad absorption bands in the spectra of the merocyanine forms of spiropyrans that we recorded, but the line connecting the experimental points has appreciable breaks. This is apparently associated with the fact that, because of the impossibility of accurately reproducing the same photosteady state in the kinetic experiments, the accuracy of the results is substantially inferior to the accuracy of the direct spectrophotometric measurements.

To smooth out the breaks on the experimental curves and to obtain the statistically most reliable results, we approximated the experimental curves by means of Gaussian curves, proceeding from the assumption that the absorption bands of the merocyanine form of the spiropyran have a normal distribution curve [16, 17]

$$\varepsilon = \varepsilon_{max} e^{-\frac{(\nu - \nu_{max})^2}{\delta^2} \ln 2},$$

where $\varepsilon_{\max}$ is the extinction coefficient at the maximum of the band ($\nu_{\max}$), and δ is the band halfwidth.

The approximation was made with an M-220 computer from a program in which the initial values of the variable parameters $\varepsilon_{\max}$, $\nu_{\max}$, and δ were computed and then refined by means of the iteration procedure of least squares using the method of coordinate descent. An example of a curve calculated by means of this method is presented in Fig. 1. The calculations demonstrated that the experimental data are satisfactorily approximated by Gaussian curves; the mean square deviation of the experimental points from the calculated values generally does not exceed 10% of the $\varepsilon_{\max}$ value.

The data obtained as a result of the calculations make it possible to determine the position of the maximum of the absorption band, the extinction coefficient at the maximum, and the band half width; they also enable one to calculate the oscillator strength of the band from the formula [16]

$$f = 0.92 \cdot 10^{-8} \varepsilon_{max} \delta.$$

The characteristics of the absorption spectra of the merocyanine forms of spiropyrans I and II in alcohol, dioxane, and toluene are presented in Table 1.

As seen from the results, two broad bands are observed in the absorption spectra of the merocyanine forms of spiropyrans. The first absorption band, which is linked with the oscillation of the charge along the long axis of the molecule [2], undergoes a very strong hypsochromic shift as the polarity of the solvent increases; in most cases, the integral intensity of the band also decreases in the process. These results are in agreement with the principles of the solvatochromic behavior of merocyanine dyes established in [18, 19] and are explained, in conformity with modern concepts of the solvatochromism of neutrocyanine dyes [20], by an increase in the contribution of polar form B_1 (see the scheme above) to the real structure of the molecule as the polarizing effect of the medium increases.

TABLE 1. Absorption Spectra of the Merocyanine Forms of Spiropyrans

Spectrum	Band I				Band II			
	λ_{max}, nm	ε_{max}	δ, cm⁻¹	f	λ_{max}, nm	ε_{max}	δ, cm⁻¹	f
Spiropyran I in toluene	586	49600	1700	0,777	383	26800	1550	0,382
Spiropyran II in toluene	598	51700	1710	0,815	368	35500	2360	0,771
Spiropyran I in dioxane	577	42600	1470	0,579	367	28600	2390	0,629
Spiropyran II in dioxane	580	86400	1610	1,279	377	49400	1700	0,771
Spiropyran I in alcohol	524	11200	1610	0,166	365	16000	3910	0,575
Spiropyran II in alcohol	527	14000	1380	0,178	380	18300	2920	0,492

The second absorption band, the nature of which, according to the data in [1], is associated with the oscillation of charge along the short axis of the molecule to the electron-acceptor NO_2 group, does not undergo such regular hypsochromic shifts as the first band as the solvent polarity increases; in addition, no substantial decrease in the intensity of the second band is observed.

It should be noted that the introduction of a fluorine atom into the 5 position of the spiropyran molecule leads to a bathochromic shift of the maximum of the absorption band in the visible region and an increase in its integral intensity. Bathochromic shifts of this type are often observed when substituents are introduced into the p position relative to the nitrogen atom of the heterocyclic part of molecules of polymethine dyes [21].

EXPERIMENTAL

A single-beam apparatus with mutually perpendicular activating and probe beams and a thermostatted cuvette holder equipped with a stirrer was used to measure the light transmission of solutions of the spiropyrans in the photosteady state. An SVD-120A mercury lamp, the radiation of which was filtered by a combination of UFS-6 and BS-7 glass filters, which isolate the 366-nm mercury line, was used as the source of activating light. The photocolorization reaction was carried out in a rectangular quartz cuvette with four transparent windows with a distance of 1 cm between the walls in the directions of the activating and probe beams. All of the measurements were made at 20 ± 0.1°.

The absorption spectra of the photocolored solutions of spiropyrans were measured in the UV and visible regions of the spectra according to points through 10 nm. A correction for light scattering from the activating source, the intensity of which was about 10% of the intensity of the probe beam and could be accurately measured during the experiment, was introduced in the 355-375 nm region.

The absorption spectra of the starting solutions were measured with an SFD-2 spectrophotometer.

Purified toluene [22], dioxane [23], and absolute ethanol, obtained by absolutizing 95% alcohol by treatment with anhydrous copper sulfate, were used as solvents.

LITERATURE CITED

1. G. I. Lashkov, M. V. Savost'yanova, A. V. Shablya, and T. A. Shakhverdov, in: Molecular Photonics [in Russian], Nauka, Leningrad (1970), p. 299.
2. J. C. Besnard, Theses l'Universite de Strasbourg (1966).
3. O. Shaudé, Cahieres de Physique, 8, 50-52 (1954).
4. M. B. Gordin and M. A. Gal'bershtam, Khim. Geterotsikl. Soedin., 425 (1971).
5. J. Hirshberg, R. Heiligman-Rim, and E. Fischer, J. Chem. Soc., 156 (1961).
6. E. Fischer, J. Phys. Chem., 71, 3704 (1967).
7. J. C. Metras, M. Mosse, and C. Wippler, J. Chim. Phys., 62, 659 (1965).
8. T. A. Shakhverdov, Teor. i Éksperim. Khim., 4, 421 (1968).
9. R. Heiligman-Rim, J. Hirshberg, and E. Fischer, J. Phys. Chem., 66, 2465, 2470 (1962).
10. A. I. Nogaideli, K. G. Dzhaparidze, M. I. Brodzeli, L. V. Devadze, D. P. Maisuradze, É. L. Kertsman, and M. Ya. Chubabriya, Coobshcheniya Akad. Nauk Gruz.SSR, 40, 607 (1965).
11. E. Berman, R. E. Fox, and F. D. Thomson, J. Am. Chem. Soc., 81, 5605 (1959).
12. G. I. Lashkov and A. V. Shablya, Optika i Spektroskopiya, 19, 821 (1965).
13. J. B. Flannery, J. Am. Chem. Soc., 90, 5660 (1968).
14. M. B. Gordin and M. A. Gal'bershtam, Khim. Geterotsikl. Soedin., 1159 (1971).
15. M. B. Gordin and M. A. Gal'bershtam, Kinetika i Kataliz, 12, 774 (1971).
16. K. B. Yatsimirskii, Spectroscopic Methods in the Chemistry of Complexes [in Russian], Khimiya, Moscow—Leningrad (1964), p. 6.
17. G. Derflinger and H. Lischka, Monatsh., 99, 1851 (1968).
18. L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt, F. L. White, H. W. J. Cressman, and S. G. Dent, J. Am. Chem. Soc., 73, 5332 (1951).
19. L. G. S. Brooker, G. H. Keyes, and D. W. Heseltine, J. Am. Chem. Soc., 73, 5350 (1951).
20. A. I. Kiprianov, Usp. Khim., 29, 1336 (1960).
21. I. M. Kogan, Chemistry of Dyes [in Russian], Moscow (1956), p. 395.
22. J. H. Mathews, J. Am. Chem. Soc., 48, 562 (1926).
23. A. Rieche, Z. Angew. Chem., 44, 896 (1931).