

PHOTOCHROMIC AND THERMOCHROMIC SPIRANES.

20.* PHOTOCHROMIC PROPERTIES OF SOLID-PHASE FILMS OF NOVEL FORMYL-SUBSTITUTED SPIROPYRANS OF THE INDOLINE SERIES

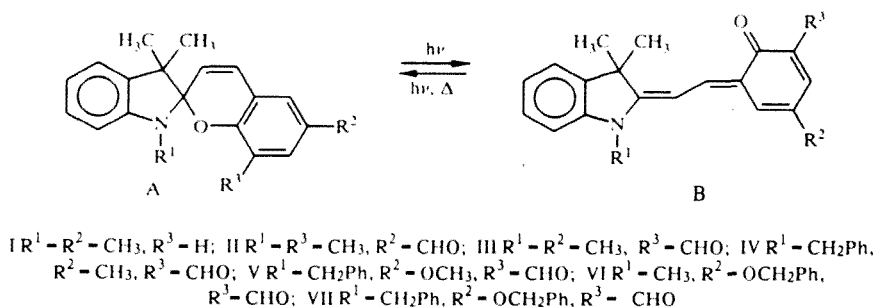
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We have synthesized novel formyl-substituted spiropyrans of the indoline series. We have obtained solid-phase amorphous films of the synthesized spiropyrans by thermal vacuum deposition and established their capacity for photochromic transformations. We have investigated the effect of the substituents on the spectral properties of the original and colored forms of the solid-phase spiropyran films. We have shown that the kinetic characteristics of the photochromic transformations of these compounds in solid-phase films depend considerably on the bulk of the substituents in the indoline and benzopyran moieties, and also their electron-active properties in the latter. Along with reversible processes, in the solid-phase spiropyran films we have observed irreversible photoreactions leading to degradation of the photochromic system.

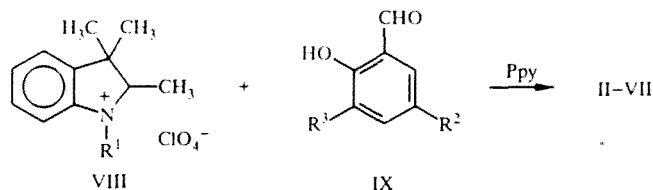
Spiropyrans are considered to be some of the most effective organic photochromes. Their photochromic properties are the basis for photo- and thermally reversible reactions of opening of the pyran ring with formation of isomeric quinoid—betaine structures [2].

Spiropyrans which have found practical application nevertheless have a number of important disadvantages connected both with their intrinsic characteristics (low photostability) and the conditions under which they are used (the acute dependence of the quantum yield and the bleaching rate on the nature of the solvent or the polymeric matrix [3]). At the present time, a great deal of attention has been focused on searching for new types of spiropyrans and investigating them under conditions providing the most efficient use of their photochromic properties. Accordingly, the use of solid-phase amorphous films obtained by thermal vacuum deposition is quite promising. An advantage of such films is that the technique for obtaining optically homogeneous samples which are quite amenable to investigation is relatively simple. From the investigator's point of view, another important factor is that the amorphous structure eliminates the effect of close crystal packing and smoothes out the strong specific intermolecular interactions characteristic for both the crystals and the solutions (including polymeric matrices) and is responsible for the dependence of the spectral and photochromic properties on the easily modified molecular structure. Nevertheless, information about photoinitiated processes in amorphous spiropyran films obtained by vacuum deposition is quite limited [4-6]. Recently it was shown [7] that the appearance of photochromic properties in indoline spiropyrans in amorphous films is favored by the presence of strong electron-acceptor groups in the 2H-chromene moiety in the 6 and (or) 8 positions. Accordingly, in this work, using the methods of steady-state spectroscopy and photochemistry, we have carried out a comparative study of the effect of the molecular structure of novel indoline spiropyrans II-VII and spiropyran I on the spectral characteristics of the original A and colored B forms, and the kinetic characteristics of photocoloration and thermal bleaching in films obtained by thermal vacuum deposition.

*For communication 19, see [1].



The spiropyrans II-VII were obtained by condensation of the perchlorate of 1-alkyl-2,3,3-trimethyl-3H-indoline VIII with substituted salicylic aldehydes IX in the presence of base.



ELECTRONIC ABSORPTION SPECTRA FOR SOLID-PHASE AMORPHOUS FILMS OF ORIGINAL PHOTOCOLORED FORMS OF SPIROPYRANS

Electronic absorption spectra of amorphous films of compounds I-VII are characterized by the longest wavelength absorption band with maximum in the 320-385 nm region (Table 1). Such a band is typical for the cyclic structure A with orthogonal, weakly interacting heteroarene and 2H-chromene moieties, and is connected with an electronic transition due to charge transfer from the $C_{\text{pyro}}-O$ group to the aryl ring of the 2H-chromene moiety [8].

In fact, the positions of the absorption bands in the spectra of spiropyrans with different substituents on the indoline moiety are practically identical (for example, compounds III and IV, VI and VII). At the same time, introduction of substituents into the chromene moiety leads to significant (for example, III and VI, IV and VII) shifts of the long-wavelength absorption band, depending on the nature of the substituent. We should also note that in amorphous films we do not observe bands connected with any aggregates of spiropyran molecules. Moreover, the absence of longer-wavelength bands also suggests that in the studied films, an equilibrium between the cyclic A and the merocyanine B structures does not occur (this equilibrium is apparent in a number of cases for solutions of spiropyrans in the ground state) [2].

From the data in Table 1 it follows that introduction of different types of substituents into the chromene part (compounds II-VII) results in a bathochromic shift of the long-wavelength band. Accordingly, the studied compounds should be separated into two groups. In the first group (compounds II-IV), introduction of a single acceptor group CHO shifts the absorption band by 15-45 nm, depending on the position of the substituent.

Introduction of an electron-donor substituent in the 6 position of the chromene part of the spiropyran in the second group of compounds (V-VII) leads to a sharp bathochromic shift of the absorption band ($\Delta\lambda = 60-65$ nm, relative to the spectrum of an amorphous film of spiropyran I).

The colored form B, in contrast to the original cyclic A with two mutually orthogonal moieties, represents a relatively flattened structure with a system of conjugated bonds. Therefore, introduction of substituents into any of the parts of this structure markedly affects the position of the long-wavelength absorption band, responsible for the color (Table 1).

Upon introduction of an acceptor group CHO in the 8 position (compound III), we observe a substantial shift of the band toward longer wavelengths compared with the spectrum of spiropyran I.

Introduction of an additional donor substituent in the 6 position (compounds V, VI) leads to a further bathochromic shift of the absorption band. Addition of a CH_2Ph group to the nitrogen atom acts like introduction of an electron-donor substituent, producing an additional bathochromic shift of the absorption band (compare with spiropyrans III and IV, VI and

TABLE 1. Spectral and Kinetic Characteristics of Solid-Phase Films of Spiropyrans I-VII

Compound	λ_{\max}^A , nm	λ_{\max}^B , nm	λ_{\max}^C , nm	η	τ , sec
I	320*	610	—	1	3.6
II	335*	584	485	0.33	640
III	366	635	488	0.94	82
IV	364	648	485	0.53	132
V	385	672	490	0.29	158
VI	381	651	485	0.55	108
VII	378	657	488	0.24	220

*Pronounced maximum is observed only in solid-phase films; in solutions, this maximum appears as a shoulder.

VII, also see compound V). On the other hand, introduction of a CHO group in the 6 position (compound II) shifts the absorption band toward shorter wavelengths relative to compound I.

Thus, the spectral characteristics of solid-phase amorphous films are completely determined by the molecular structure of the original A and the colored B forms of the spiropyrans.

EFFICIENCY OF THE PHOTOCOLORATION REACTION

Photocoloration of solid-phase amorphous films of spiropyrans I-VII occurs upon irradiation at the long-wavelength absorption band of the original cyclic form A of the spiropyran molecule, as a result of the appearance of an absorption band for the quinoid-betaine structure B in the visible region of the spectrum.

The data obtained on the relative efficiencies of the photoprocess for the formation of the colored form in films of spiropyrans I-VII are presented in Table 1. In considering these data, we need to bear in mind that in solid-phase films, each spiropyran molecule is found in an environment forming the "free volume" within which structural evolutions of the given molecule occur. For the formation of a colored structure of type B, at least two stages must be accomplished: breaking of the $C_{\text{spiro}}-\text{O}$ bond and *cis-trans* isomerization. Under conditions for the existence of the dark recyclization reaction, the difficulty of the process of *cis-trans* isomerization (due to steric interaction between bulky substituents R^1 and R^2 and the environment) leads to reduction in the observed efficiency of photocoloration. Since isomerization may occur as a result of rotations of one part of the molecule relative to the other, bulky substituents ($R^1, R^2 = \text{CH}_2\text{Ph}$) in only one of the moieties (the indoline moiety (compound IV) or the benzopyran moiety (compound VI)) do not lead to a substantial difference in the efficiency of photocoloration. In the case of spiropyran VII, when bulky substituents are included in both parts of the molecule, the efficiency of photocoloration is the lowest.

While steric factors exert the predominant effect in the stage of *cis-trans* isomerization for the process of formation of the colored structure B in amorphous films, the effect of the electronic characteristics of the substituents R^2, R^3 predominates in the stage of breaking the $C_{\text{spiro}}-\text{O}$ bond. The efficiency of photocoloration for all the studied films of formyl-substituted spiropyran II-VII is lower than for the unsubstituted spiropyran I, since the formyl group in the 6, 8 positions reduces the efficiency of photoinitiated breaking of the $C_{\text{spiro}}-\text{O}$ bond. The presence of the electron-donor group OCH_3 (compound V) leads to additional reduction of the efficiency of photocoloration (in particular, compared with compound IV, distinguished from spiropyran V by the substituent $R_2 = \text{CH}_3$).

LIFETIME AND STABILITY OF COLORED FORMS

Dark bleaching of solid-phase amorphous films (the drop in the intensity of the absorption band of the colored form after the irradiation is stopped) occurs in all cases practically according to an exponential law. The lifetime (τ) varies within the range from a few seconds to tens of thousands of seconds (Table 1) as the substituent is varied.

The recyclization process includes a stage of *trans*–*cis* isomerization, so the steric effect of bulky substituents in both parts of the spiropyran molecule on the lifetime of the colored form is of the same nature as the effect on the observed efficiency of photocoloration. Bulky substituents, hindering *trans*–*cis* isomerization, increase the lifetime of the colored form. Thus for the spiropyran III with $R^1 = R^2 = \text{CH}_3$, the lifetime is 82 sec; and for compounds IV, V, VI with bulky substituents ($R^1, R^2 = \text{CH}_2\text{Ph}$) on one of the moieties of the spiropyran molecule, the lifetime is 132, 158, and 108 sec respectively. In the case of compound VII with bulky substituents on both parts of the spiropyran ($R^1 = R^2 = \text{CH}_2\text{Ph}$), the lifetime is equal to 220 sec.

In contrast to the forward photoreaction, where the efficiency of photocoloration is affected considerably by steric interactions, dark bleaching to a large degree is determined by the electronic characteristics of the substituents R^2, R^3 , variation of which probably leads to a change in the thermodynamic stability of the most energetically favorable acyclic isomers.

As we see from the data presented, the lifetime of form B increases considerably in the series I, III, II (Table 1).

Thus, the dependence of the lifetime of the colored form on the nature of the substituents is determined both by intramolecular electronic and intermolecular steric interactions in an amorphous medium, which lead to kinetic stabilization of the most stable *trans*-merocyanine structure.

PHOTODEGRADATION

Upon prolonged irradiation ($t_{\text{irr}} > 10^4$ sec), amorphous films of spiropyrans I-VII lose their photochromic properties. In this case, irreversible changes (photodegradation) occur in the films, possibly connected with degradation of the spiropyran molecules and leading to the formation of the thermally stable compound C, characterized by absorption with maximum in the 485–490 nm region (Table 1).

EXPERIMENTAL

The PMR spectra were recorded on a Unity-300 instrument in CDCl_3 solution. Solid-phase films of spiropyrans I-VII were obtained by thermal vacuum deposition on a VUP-4 apparatus with residual pressure $2 \cdot 10^{-5}$ torr. As the substrates, we used quartz plates. The electronic absorption spectra were recorded on a Specord M-40 spectrophotometer. For the photochemical investigations, we used a radiation source with a DRSh-250 mercury lamp and a set of light filters for isolating lines of the mercury spectrum. The kinetic curves for photocoloration were recorded at the selected wavelength (at the maxima of the absorption bands for the colored forms of spiropyrans I-VIII) directly upon irradiation with light at 313 nm on an apparatus assembled on the base of an Hitachi Perkin-Elmer 139 spectrophotometer. We recorded the dark bleaching curves on the same apparatus.

In order to estimate the efficiency of photocoloration, we used the parameter η , which is the ratio of the quantum yields of the test spiropyran Φ and the reference spiropyran 1',3',3',6-tetramethylspiro[2H-1-benzopyran-2,2'-indoline] Φ_1 :

$$\eta = \Phi/\Phi_1 \quad (1)$$

In low-temperature investigations (77K) in a glass-forming solvent (isopentane–isopropyl alcohol, 4:1), when the process of thermal recyclization does not occur, we established that photochemical bleaching is accomplished in a time ($\tau_{1/2} \sim 10^4$ sec) considerably longer than for photocoloration ($\tau_{1/2} \sim 10$ sec) for comparable intensities of the activating radiation. Furthermore, photolysis of the samples was done at a wavelength of 313 nm in the region where the intensity of the S_0 – S_2 transition of the colored forms of the spiropyrans is lower than in the 330–370 nm region, where this transition is predominantly localized. So the backward photoreaction can be neglected when determining the efficiency of photocoloration of solid-phase amorphous films of spiropyrans I-VII.

From the photocoloration curves for the spiropyran films, recorded at the absorption maxima of the colored forms under identical irradiation conditions, $D = f(t_{\text{irr}})$, we constructed the curves $D/D_{\infty} = f(t_{\text{irr}})$, where D_{∞} is the maximum equilibrium value of the optical density achievable under the given irradiation conditions. Then we determined the slope of the $D/D_{\infty} = f(t_{\text{irr}})$ curve at the initial moment of time, which for the considered reaction of the type $A \rightleftharpoons B$ represents the sum of

the rate constants for the forward photolytic reaction (k_{ph}) and the backward thermal reaction ($k\Delta$). On the other hand, the quantum yield of the photoreaction by definition is:

$$\Phi = (-d[A]/dt)/I_{abs} \quad (2)$$

where $[A]$ is the concentration of the original compound, I_{abs} is the intensity of the absorbed light.

$$I_{abs} = I_0(1 - 10^{-\epsilon[A]l}) S \quad (3)$$

here I_0 is the intensity of the incident radiation; ϵ is the molar extinction coefficient at the irradiation wavelength; l is the thickness of the absorbing layer; S is the surface area on which the radiation is incident. In the case when the optical density at the irradiation wavelength is less than 0.1, we can write:

$$I_{abs} = 2.303 I_0 \epsilon[A] l S \quad (4)$$

for unit volume, thus:

$$-d[A]/dt = 2.303 I_0 \Phi \epsilon [A] \quad (5)$$

or:

$$-d[A]/dt = k'_{ph} [A] \quad (6)$$

where

$$k'_{ph} = 2.303 I_0 \Phi \epsilon \quad (7)$$

In this case, when the photocoloration process $A \rightleftharpoons B$ for films of compounds I-VII is accomplished in a time on the order of 10 sec, and photobleaching and photodegradation appear in approximately 10^4 sec, we can assume that the rate constant for accumulation of the photoproduct B is equal to the rate constant for loss of the original compound (A) — $k_{ph} = k'_{ph}$. And thus, determining ϵ at the irradiation wavelength (313 nm), we obtain η from Eq. (1). The values of the molar extinction coefficients for the estimate of the efficiency of the photoreaction in films of compounds I-VII are obtained from the absorption spectra of solutions of the spiropyran in toluene.

As the adsorbent for preparative chromatography, we used Al_2O_3 (neutral, standard Brockmann activity II).

The elemental analysis data for the synthesized compounds (C, H, and N) correspond to the calculated values.

1',3',3',6-Tetramethylspiro[2H-1-benzopyran-2,2'-indoline] (I) was synthesized according to the technique published in [9].

1',3',3',8-Tetramethyl-6-formylspiro[2H-1-benzopyran-2,2'-indoline] (II, $C_{21}H_{21}NO_2$). A mixture of 1.37 g (5 mmole) perchlorate VIII ($R^1 = CH_3$) and 0.82 g (5 mmole) aldehyde IX ($R^2 = CHO$, $R^3 = CH_3$) in 25 ml 2-propanol was heated to boiling; 0.43 g (5 mmole) piperidine was added and this was boiled for 1 h. The reaction mixture was cooled, poured into 30 ml water, and extracted with ether. The extract was washed with water and dried with sodium sulfate. The ether was evaporated and the residue was chromatographed on a column with Al_2O_3 (2×40 mm, eluent $CHCl_3$). Yield, 0.93 g (58%). T_{mp} 145-146°C (from heptane). PMR spectrum: 1.14 (3H, s, 3'-CH₃), 1.22 (3H, s, 3'-CH₃), 1.96 (3H, s, 8-CH₃), 2.66 (3H, s, 1'-CH₃), 5.76 (1H, d, $J = 10$ Hz, 3-H), 6.50-7.46 (7H, m, 4-H, H_{arom}), 9.81 ppm (1H, s, 6-CHO).

1',3',3',6-Tetramethyl-8-formylspiro[2H-1-benzopyran-2,2'-indoline] (III, $C_{21}H_{21}NO_2$). Obtained as for spiropyran II from 1.37 g (5 mmole) perchlorate VIII ($R^1 = CH_3$) and 0.82 g (5 mmole) aldehyde IX ($R^2 = CH_3$, $R^3 = CHO$). Yield, 0.89 g (56%). T_{mp} 105-106°C (from ethanol). PMR spectrum: 1.12 (3H, s, 3'-CH₃), 1.25 (3H, s, 3'-CH₃), 2.16 (3H, s, 6-CH₃), 2.68 (3H, s, 1'-CH₃), 5.78 (1H, d, $J = 10$ Hz, 3-H), 6.49-7.42 (7H, m, 4-H, H_{arom}), 10.06 ppm (1H, s, 8-CHO).

1'-Benzyl-3',3',6-trimethyl-8-formylspiro[2H-1-benzopyran-2,2'-indoline] (IV, $C_{27}H_{25}NO_2$). Obtained as for spiropyran II from 1.25 g (5 mmole) perchlorate VIII ($R^1 = CH_2Ph$) and 0.82 g (5 mmole) aldehyde IX ($R^2 = CH_3$,

$R^3 = \text{CHO}$). Yield, 1.05 g (53%). T_{mp} 127-128°C (from heptane). PMR spectrum: 1.26 (3H, s, 3'-CH₃), 1.31 (3H, s, 3'-CH₃), 2.17 (3H, s, 6-CH₃), 4.13 (1H, d, $J = 15$ Hz, 1'-CH₂Ph), 4.52 (1H, d, $J = 15$ Hz, 1'-CH₂Ph), 5.79 (1H, d, $J = 10$ Hz, 3-H), 6.21-7.38 (12H, m, 4-H, H_{arom}), 10.09 ppm (1H, s, 8-CHO).

1'-Benzyl-3',3'-dimethyl-6-methoxy-8-formylspiro[2H-1-benzopyran-2,2'-indoline] (V, C₂₇H₂₅NO₃). Obtained as for spiropyran II from 1.75 g (5 mmole) of perchlorate VIII ($R^1 = \text{CH}_2\text{Ph}$) and 0.9 g (5 mmole) aldehyde IX ($R^2 = \text{OCH}_3$, $R^3 = \text{CHO}$). Yield, 0.99 g (48%). T_{mp} 161-162°C (from heptane). PMR spectrum: 1.26 (3H, s, 3'-CH₃), 1.32 (3H, s, 3'-CH₃), 3.72 (3H, s, 6-OCH₃), 4.13 (1H, d, $J = 15$ Hz, 1'-CH₂Ph), 4.51 (1H, d, $J = 15$ Hz, 1'-CH₂Ph), 5.83 (1H, d, $J = 10$ Hz, 3-H), 6.21-7.22 (12H, m, 4-H, H_{arom}), 10.09 ppm (1H, s, 8-CHO).

6-Benzoyloxy-1',3',3'-trimethyl-8-formylspiro[2H-1-benzopyran-2,2'-indoline] (VI, C₂₇H₂₅NO₃). Obtained similarly as for spiropyran II from 1.37 g (5 mmole) perchlorate VIII ($R^1 = \text{CH}_3$) and 1.28 g (5 mmole) aldehyde IX ($R^2 = \text{OCH}_2\text{Ph}$, $R^3 = \text{CHO}$). Yield, 0.83 g (41%). T_{mp} 47-48°C (from hexane). PMR spectrum: 1.12 (3H, s, 3'-CH₃), 1.26 (3H, s, 3'-CH₃), 2.70 (3H, s, 1-CH₃), 4.98 (2H, s, 6-OCH₂Ph), 5.81 (1H, d, $J = 10$ Hz, 3-H), 6.45-7.32 (12H, m, 4-H, H_{arom}), 10.08 ppm (1H, s, 8-CHO).

1'-Benzyl-6-benzoyloxy-3',3'-dimethyl-8-formylspiro[2H-1-benzopyran-2,2'-indoline] (VII, C₃₃H₂₉NO₃). Obtained as for spiropyran II from 1.75 g (5 mmole) perchlorate VIII ($R^1 = \text{CH}_2\text{Ph}$) and 1.28 g (5 mmole) aldehyde IX ($R^2 = \text{OCH}_2\text{Ph}$, $R^3 = \text{CHO}$). Yield, 1.10 g (45%). T_{mp} 61-62°C (from hexane). PMR spectrum: 1.24 (3H, s, 3'-CH₃), 1.32 (3H, s, 3'-CH₃), 4.13 (1H, d, $J = 15$ Hz, 1'-CH₂Ph), 4.52 (1H, d, $J = 15$ Hz, 1'-CH₂Ph), 4.97 (2H, s, 6-OCH₂Ph), 5.84 (1H, d, $J = 10$ Hz, 3-H), 6.24-7.37 (12H, m, 4-H, H_{arom}), 10.08 ppm (1H, s, 8-CHO).

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REFERENCES

1. B. S. Luk'yanov, N. B. Ivanov, L. E. Nivorozhkin, V. I. Minkin, and G. S. Borodkin, *Khim. Geterotsikl. Soedin.*, No. 9, 1253 (1995).
2. R. Guglielmetti, in: *Photochromism: Molecules and Systems*, H. Durr and H. Bouas-Laurent (eds.), Elsevier, Amsterdam (1990), p. 314.
3. R. C. Bertelson, in: *Techniques in Chemistry*, G. H. Brown (ed.), Wiley, New York (1971), p. 45.
4. T. Nakayama, I. Shimizu, H. Kakado, and E. Inone, *Bull. Chem. Soc. Jpn.*, **44**, 3203 (1971).
5. T. Yoshida, A. Mivnaka, and N. Funakoshi, *J. Chem. Soc. Chem. Commun.*, No. 2, 437 (1986).
6. T. Yoshida, A. Mivnaka, and N. Funakoshi, *Thin Solid Films*, **162**, 343 (1986).
7. V. Minkin, *Mol. Cryst. Liq. Cryst.*, **246** (1994).
8. R. V. Blok, *Zh. Fiz. Khim.*, **52**, 1683 (1978).
9. A. Hinnen, C. Audic, and R. Gantron, *Bull. Soc. Chim. France*, No. 5, 2066 (1968).