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PHOTOCHROMISM. SYNTHESIS AND PROPERTIES OF INDOLINOSPIROBENZOTHIOPYRANS

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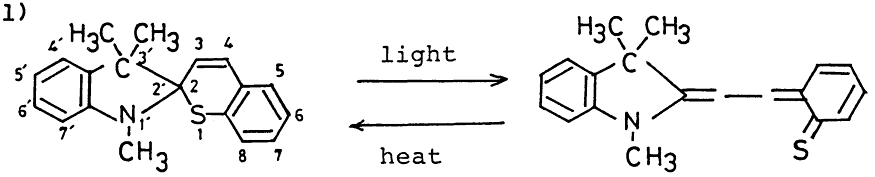
Novel photochromic compounds, indolinospirobenzothiopyrans, were prepared and their properties in polymer films were examined. The absorption bands of the colored form lie around 100 nm deeper in the long-wave region of the spectrum than are the case with the common spiropyrans.

The spiropyrans belong to one of the most well-investigated classes of photochromic materials, being distinguished by their high resolution and ease of information storage and retrieval. At the present time, however, the demand is for the development of photochromic systems in which the absorption band of the colored form is in the longer-wavelength region of the spectrum than is the case with the common spiropyrans, particularly for applications using laser diodes (wavelength; ≈800 nm) for recording and retrieval.

An attempt to obtain a long-wavelength absorption for the merocyanine form by synthesizing a compound containing the benzothiopyran ring was first made by Becker and Kolc.1)



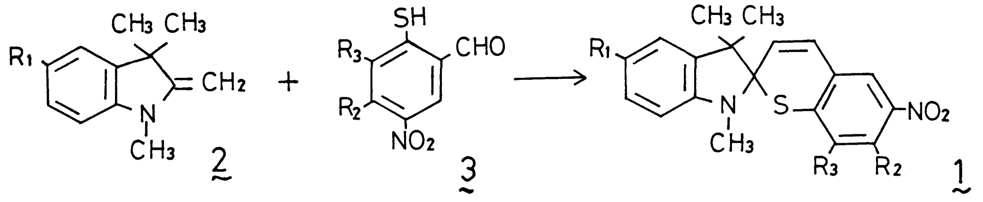
(colorless) (colored)

Scheme 1.

They showed that the colored form of 1',3',3'-trimethylspiro[2H-1-benzothiopyran-2,2'-indoline], had a strong absorption band in the wavelength region of 600-850 nm in 3-methylpentane at 77 K, but that the merocyanine form was not produced at room temperature either in solution or in a polymer film.

In order to obtain photochromic compounds whose colored forms have a strong absorption band in the wavelength region of 700-850 nm and are stable even at room temperature, we synthesized indolinospirobenzothiopyrans with a nitro group at the 6-position.

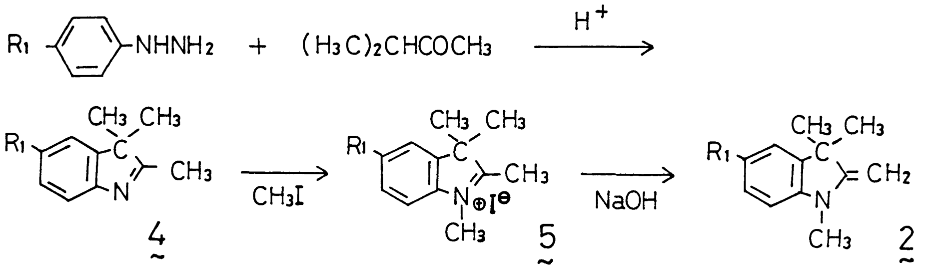
Indolinospirobenzothiopyrans (1) with a nitro group at the 6-position were synthesized by the reaction of 1,3,3-trimethyl-2-methyleneindolines (2) and 5-nitrosalicylaldehydes (3) in ethanol (Scheme 2).



Scheme 2.

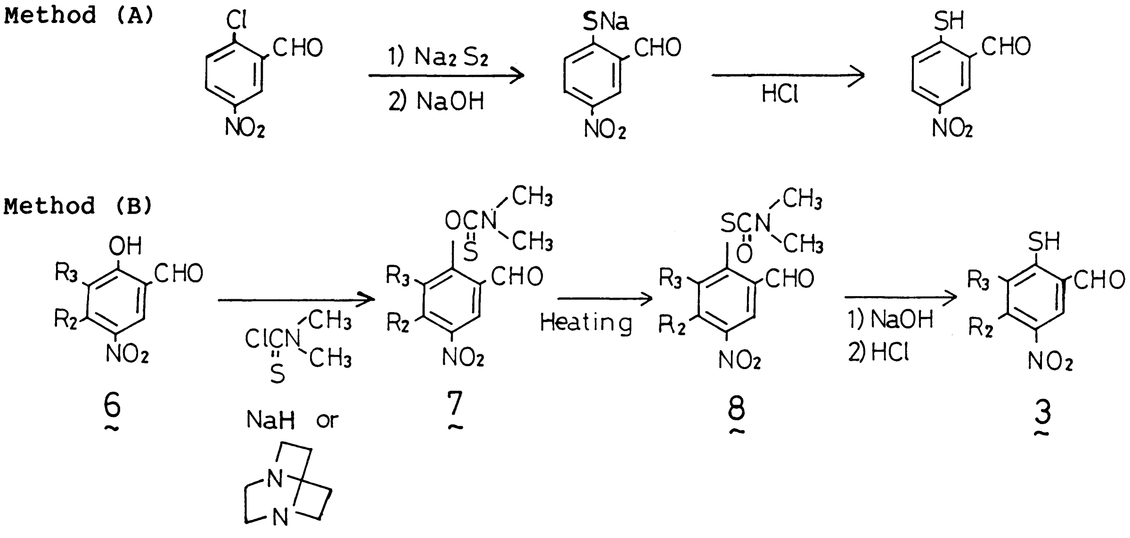
The compounds 2 are prepared according to reaction Scheme 3, by methylation of 2,3,3-trimethylindolenines 4 at the N-position with methyl iodide to give indolenium salts 5 and subsequently treating the resulting salts with an alkali.

The compounds 4 were usually obtained on the basis of the Fischer's indole synthesis in which substituted phenylhydrazines or their hydrochloride salts and 3-methyl-2-butanone were heated under acidic conditions (Scheme 3).$^{2)}$



Scheme 3.

The 5-nitrothiosalicylaldehydes 3 were prepared by the following two methods: (A) conversion of a halogen atom of o-chlorobenzaldehyde into an SH group$^{3)}$; (B) conversion of an OH group of salicylaldehyde into an SH group (Scheme 4).$^{4)}$



Scheme 4.

Method (A) could be applied only to the preparation of 5-nitrothiosalycylaldehyde, because the starting o-chlorobenzaldehydes with various substituents were not readily available. On the other hand, the method (B) is excellent for the preparation of 5-nitrothiosalicylaldehyde derivatives, because the starting salicylaldehydes are easily prepared and the yield in each reaction is very high.

In Method (B), dimethylthiocarbamates **7** were first prepared, followed by heating for the rearrangement reaction of O and S to give the compounds **8** and subsequent alkaline hydrolysis to give thiosalicylaldehydes **3**.

The synthesized indolinospirobenzothiopyrans are shown in Table 1. The structures were determined by ^{1}H-NMR,IR, mass spectra, and elemental analyses.5)

Table 1. Synthesis and property of indolinospirobenzothiopyrans **1**

Spiropyrans **1**			Yield/%	Mp θm/°C	Absorption	Substituent constant	
R_1	R_2	R_3			λ_{max}/nm	σ_i	σ_b
H	H	H	35	180-180.5	680	0	0
NO_2	H	H	87	221-223	750	0.79	
Cl	H	H	29	139-139.5	690	0.12	
CH_3	H	H	44	137-138	670	-0.30	
OCH_3	H	H	31	160-162	660	-0.78	
OCH_3	H	OCH_3	79	165-166	690		-0.41
OCH_3	H	CH_3	70	177-178	675		-0.17
OCH_3	OCH_3	H	67	193-194	650		0.05
OCH_3	H	Cl	72	168-169	650		0.20
OCH_3	H	Br	41	193-194	645		0.21

The indolinospirobenzothiopyrans were dissolved with vinyl chloride-vinylidene chloride copolymer in a mixed solvent of cyclohexanone-tetrahydrofuran. The resulting solution was spin-coated onto a quartz glass plate and dried to obtain a photosensitive film of around 1 micron thickness.

The film obtained was exposed to UV light (≈360 nm). The light-yellow film changed to dark-green in color. The absorption spectrum of the spirobenzothiopyran **1** (R_1= R_2= R_3= H) is shown in Fig. 1. The non-irradiated film (a) has no absorption in the wavelength region of 500-900 nm, but the irradiated film (b) has a absorption maximum (λ_{max}) at 680 nm and the absorption extends to about 900 nm. On the other hand, in the case of the common spiropyran, 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline], the absorption of the colored film (c) has a λ_{max} at 580 nm and the absorption on the long-wave side extends only to 700 nm. Thus, it was found that the substitution of sulfur for oxygen at the 1-position of spiropyran caused dramatic red shifts more than 100 nm.

The effect of substituents on the absoption maxima in the colored polymer films was also investigated. It was found that using Brown's σ_p^+-relationship for the 5'-positions of the indolinic substitution (σ_i), and Brown's σ_m^+-relationship and Taft's σ^* values for the 7- and 8-positions ,respectively, of benzothiopyranic substitution (σ_b),6) a good correlation between λ_{max} and the substituent constants was obtained. That is, as σ_i increases or σ_b decreases,

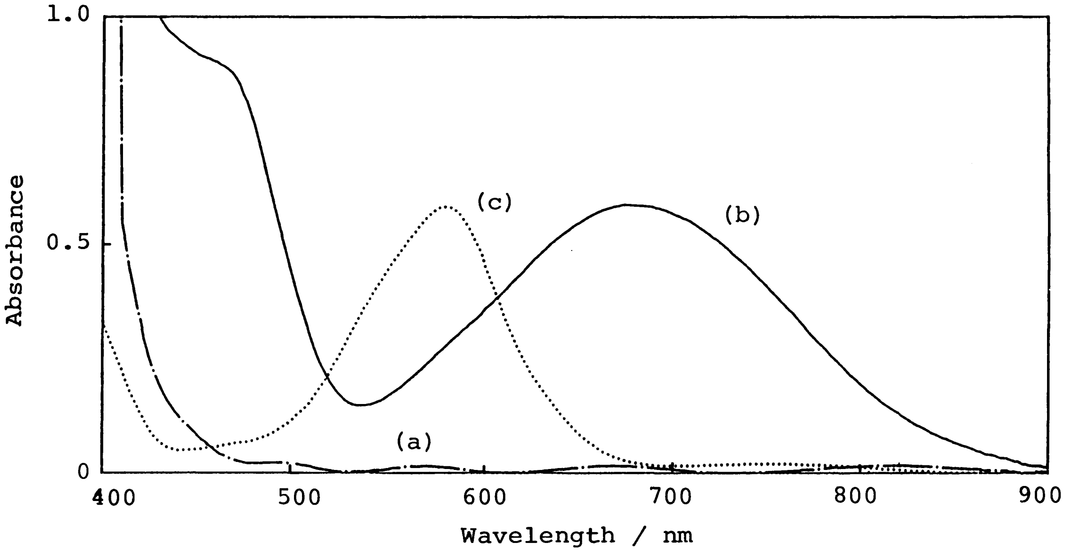


Fig.1. The absorption spectra of the photochromic polymer films.
(a) before exposure, (b) after exposure to UV light for the film of 6-nitro-1',3',3'-trimethylspiro[2H-1-benzothiopyran-2,2'-indoline], and
(c) after exposure to UV light for the film of spiropyran of the common type.

the absorption maximum shifts to longer wavelengths, as indicated in Table 1.

The colored forms could be also stabilized by varing substituents R_1-R_3 of the spirothiopyrans **1**, so that the half-life of the colored state at 30 °C was improved to more than one month. The colored forms could be bleached by heating to 80-100 °C, or by irradiation with a laser diode of 780 nm wavelength and 10 mW power. The coloring and bleaching cycles could be repeated more than one hundred times in a degassed solution. The irradiation of a weak laser beam less than 1 mW for reading the recording signals did not affect the colored form.

Further papers will deal with the effect of substituents on thermal stability, and with a detailed investigation of the photochromic behavior of these indolinospirobenzothiopyrans.

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5) **1** (R_1=R_2=R_3=H): ^{1}H-NMR ($CDCl_3$) δ 1.24(s,CH_3,3H), 1.40(s,CH_3,3H), 2.64(s,CH_3,3H), 5.96(d,CH,1H), 6.44(d,CH,1H), 6.6-7.4(m,aromatic,5H), and 7.7-8.1(m,aromatic,2H). Found: C, 67.43; H, 5.36; N, 8.28;S, 9.47%. Calcd for $C_{19}H_{18}N_2O_2S$: C, 67.0; H, 5.3; N, 8.3; S, 9.4%.
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