Effects of Substituents on the Indoline Ring on the Negative Photochromic Properties of Spirobenzopyran Derivatives

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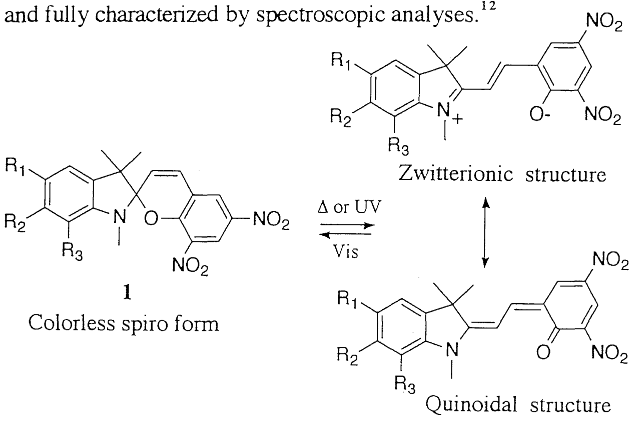
Novel substituted - 6, 8 - dinitro - 1', 3', 3' - trimethylspiro [2H - 1- benzopyran - 2 , 2' - indoline] derivatives have been synthesized in high yields, and their properties are investigated. The absorption maxima of the ring-open forms and the negative photochromic properties of spirobenzopyrans significantly depend on the substituents in the indoline ring and on the nature of the solvent used.

The photochromism of spirobenzopyrans has been investigated by many chemists since it was first discovered by Fischer and Hirshberg in 1952.[1] Much attention has been paid to photochromic spirobenzopyrans due to their applications to photoinformation memory [2] and to photoregulation of polymers' chemical and physical properties such as viscosity,[3] surface wettability,[4] surface potential [5] and surface pressure.[6] Moreover, negative photochromic spirobenzopyrans are applied to thermo-reversible imaging media[7] as well as photomemory devices. In the 1950's, Koelsch and Workman reported that 6, 8- dinitro- 1', 3', 3' - trimethylspiro [2H- 1- benzopyran - 2, 2' - indoline] **1a** showed negative photochromism in organic solvent.[8] Recently, Miyashita et al. have reported synthesis and negative photochromism of spirobenzopyrans having selenium atoms in the framework.[9] However, no extensive study of negative photochromic spirobenzopyrans has been carried out. Negative photochromic spirobenzopyrans are usually colored in both solid and solution because the colored ring-open forms of spirobenzopyrans are more thermodynamically stable than the colorless spiro forms.[10] It is generally accepted that the colored ring-open forms have the electronic configuration of a resonance hybrid, i. e., zwitterionic structure and quinoidal structure, depending on substituents and the nature of the solvent used. A solution of the colored ring-open form is bleached by irradiation with visible light corresponding to the absorption maximum and then again exhibits initial color thermally or by irradiation with UV light. The process that takes place in the negative photochromic system is presented in Scheme1. This paper reports the effects of substituents on the indoline ring on the absorption maxima and the negative photochromic properties. All of spirobenzopyrans **1** used in this research were prepared according to the general method.[11] The synthesized spirobenzopyrans **1** were purified by thin-layer chromatography and fully characterized by spectroscopic analyses.[12]



Scheme 1.

Table 1. Yields, Mp, MS spectra, Appearances and Negative Photochromic Properties of Spirobenzopyran Derivatives **1**

Spirobenzopyran derivatives 1				Yield	Mp[a]	MS (EI)	Appearance	in $CHCl_3$	in Acetone	in DMSO
Comp. No.	R_1	R_2	R_3	%	°C	m/z (M^+)		λ_{max} nm	λ_{max} nm	λ_{max} nm
1a	H	H	H	92	280 ~ 283	367	dark green	558	534	526
1b	CH_3	H	H	90	283 ~ 284	381	dark purple	559	535	528
1c[10]	OCH_3	H	H	92	274 ~ 275	401	dark purple	564	536	524
1d	F	H	H	90	210 ~ 212	385	dark green	562	535	526
1e	Br	H	H	90	224 ~ 226	445	dark purple	571	543	535
1f	H	-CH=CH-CH=CH-		95	259 ~ 260	417	dark green	581	543	534
1g	Br	-CH=CH-CH=CH-		93	288 ~ 290	495	dark green	593	553	542
1h	CH_3	H	CH_3	92	230 ~ 232	395	dark green	557	531	522
1i	F	H	F	88	277 ~ 279	403	dark green	570	540	531
1j	Br	H	Br	85	197 ~ 198	525	yellow	581[b]	552[b]	543

[a] Melting points were uncorrected. [b] The colored ring-open form was obtained by UV irradiation of the colorless spiro form of **1j** .

Spirobenzopyran derivarives, except for **1j**, colored to green or purple in solid state and exhibited negative photochromism in various organic solvents. Figure 1 illustrates the absorption spectral change of a chloroform solution of **1g**. The ring-open form of **1g** showed the broad absorption band in the 500~640 nm region. Irradiation of the chloroform solution with visible light turned it to a pale yellow solution.

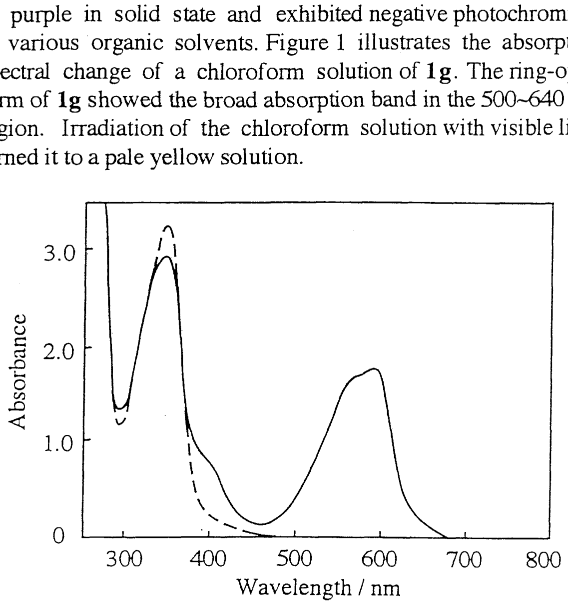


Figure 1 . Absorption spectral change of compound **1g** in chloroform under the aerial atmosphere : (—) original sample ; (---) after irradiation with visible light (λ > 500 nm).

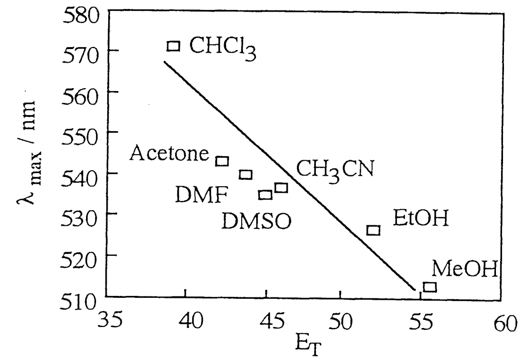


Figure 2 . Absorption maxima of compound **1e** in several polar solvents as a function of Dimroth's solvent polarity parameter, E_T.

Table 1 summarizes yields, melting points, MS spectra, appearances, and absorption maxima (λ_{max}) of the ring-open forms. Figure 2 shows the change in the absorption maximum of the ring-open form of **1e** as a function of Dimroth's parameter for solvent polarity, E_T.[13] As the solvent polarity was increased, a hypsochromic shift was observed. This blue shift of λ_{max} shows that a marked solvatochromism is exhibited by the ring-open form of the zwitterionic structure. The substituent group on the indoline ring had a significant effect on the absorption maxima of the ring-open forms of **1** . The λ_{max} of the ring-open forms of **1** became longer as the electron accepting ability of the 5'- and 7'- positions of the indoline ring increased. The ring-open form of **1j** exhibited a red shift in chloroform 23 nm longer than that of **1a** . The λ_{max} of the ring-open forms, however, remained almost constant when the indoline ring was substituted with electron donating group. On the other hand, the ring-open form of **1f** exhibited a red shift of 23 nm in chloroform compared with that of **1a**. This is because the conjugation is spread by the condensing benzene ring at the 6'- and 7'- positions of the indoline ring. Furthermore, the ring-open form of **1g** introduced bromine at the 5'- position of **1f** showed an absorption maximum at the longest wavelength, 593 nm in chloroform, which is 35 nm longer than that of **1a**.

The negative photochromism of **1e** and **1j** significantly depended on the nature of the solvent used. **1e** had a colored ring -open form in solid state; however, its equilibrium gradually shifted far to the colorless spiro form when dissolved in chloroform. Although **1e** was in equilibria between colored and colorless forms in acetone, the colored form was much more stable than the colorless form in a polar solvent such as DMSO. On the other hand, **1j** had a spiro form in solid state and exhibited photochromism in chloroform and acetone; however, it indicated negative photochromism in DMSO. It is assumed that **1j** has a spiro form in solid state and in weak polar solvents because bromo groups of the 5'- and 7'- positions of the indoline ring destabilize the quaternary N-cation of the zwitterionic structure. Nevertheless, the negative photochromism of **1j** in DMSO may be due to the stabilization of the ring-open form of the zwitterionic structure by interaction with the solvent dipole.

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References and Notes

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