CHEMISTRY LETTERS, pp. 209-212, 1991.

Synthesis and Metastable Structure of New Photochromic Spiroindolinobenzothiopyrans

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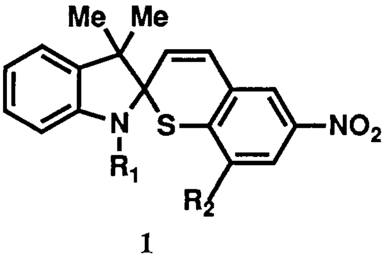
Photochromic spiroindolinobenzothiopyrans having a methacryloxymethyl group have been prepared and their colored forms were demonstrated to be a zwitterionic structure on the basis of the spectroscopic data.

Spiropyrans as one of the most typical photochromic compounds have been widely studied because of their potential utilities for photo-information memory devices. Interestingly, those having a sulfur atom in their molecular framework were reported to have the absorption maxima of the colored form within the range of the diode laser wavelength.[1,2] Although much efforts have been currently focused on the development of new spiropyrans having more efficient photochromic properties, the unstable colored structure of spirobenzothiopyrans remains unexplored because of their thermal instability.[1,2]

In this paper, we report the synthesis of a series of new spiroindolinobenzothiopyrans **1** possessing a methacryloxymethyl group at 8'-position, and describe their photochromic properties by discussing their possible structures for the unstable colored form on the basis of low temperature NMR studies and isolation of photo-induced intermediates.

Spiropyrans **1a-d** were basically prepared starting from 2,3,3-trimethylindolenine as outlined in the scheme. 5-Nitrosalicylaldehyde reacted with chloromethyl methyl ether in the presence of aluminum trichloride to yield 3-chloromethyl-5-nitrosalicylaldehyde (**2**). Then, 3-methacryloxymethyl-5-nitrosalicylaldehyde (**3**) which was given by the reaction of **2** with silver methacrylate in refluxing toluene, was converted to 3-methacryloxymethyl-*O*-(*N*,*N*-dimethylthiocarbamoyl)-5-nitrosalicylaldehyde (**4**)[3] in DMF at room temperature. The rearrangement of the thiocarbamoyl group of **4** was performed in refluxing toluene to form 3-methacryloxymethyl-*S*-(*N*,*N*-dimethylcarbamoyl)-5-nitrosalicylaldehyde (**5**)[4] which was purified by a column chromatography (SiO_2). Then, **5** was hydrolyzed with aqueous sodium hydroxide at 20 °C to yield 3-methacryloxymethyl-5-nitrothiosalicylaldehyde (**6**).[6] On the other hand, *N*-substituted 3,3-dimethyl-2-



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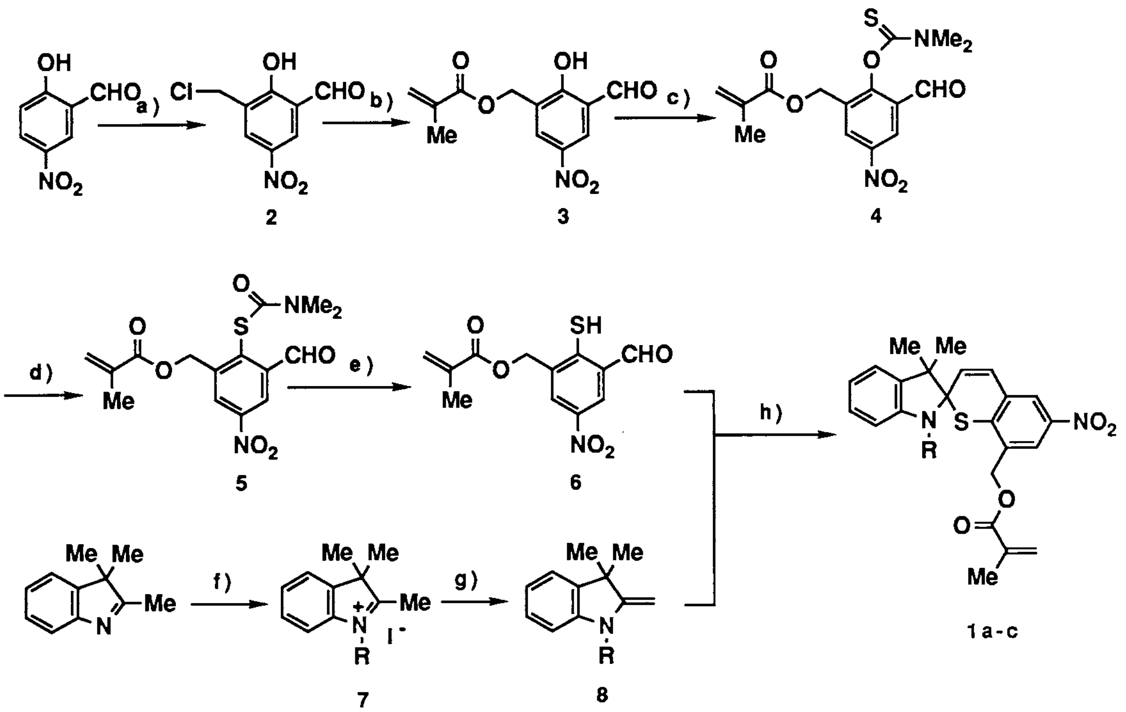
	R_1	R_2
1a	Me	$CH_2OCOC(Me)=CH_2$
1b	$CH(Me)_2$	$CH_2OCOC(Me)=CH_2$
1c	n-$C_{18}H_{37}$	$CH_2OCOC(Me)=CH_2$
1d[5]	n-$C_{18}H_{37}$	$CH_2OCO(CH_2)_{20}Me$

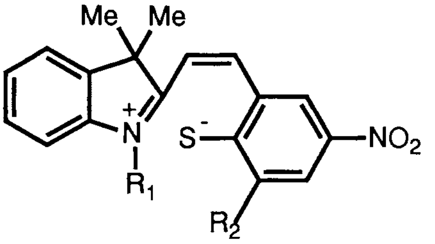


a) $MeOCH_2Cl/AlCl_3$, b) $CH_2=C(Me)COOAg$, c) Me_2NCSCl/1,4-diazabicyclo[2.2.2]octane, d) refluxed in toluene, e) equimolar 0.7 mol dm^{-3} NaOH in methanol at 20 °C under nitrogen, then 1 mol dm^{-3} HCl aq., f) R-I, g) 1 mol dm^{-3} KOH at r.t., h) refluxed in 2-butanone

methyleneindoline derivatives **8** were derived from 2,3,3-trimethylindolenine by the initial treatment with alkyl iodides, and then with a base. 8'-Methacryloxymethyl-3,3-dimethyl-6'-nitrospiro[(2'*H*)-1'-benzothiopyran-2,2'-indoline] **1a-c** were cleanly prepared as light yellow crystals by condensation of **6** with **8** in refluxing 2-butanone. The related behenoyloxymethyl derivative **1d** could be afforded by the similar manner. These compounds **1** were characterized by ^1H NMR , IR and MS spectra.[7] The yields of **1a-d** based on **6** were 49, 41, 36, and 35%, respectively.

On exposure of the light yellow solution of **1** to UV light at room temperature, rapid color change to green was observed . Facile photo-bleaching took place by exposing the colored solution to visible light (>500 nm) even at 0 °C. These photochromic properties of a series of spirobenzothiopyrans were tabulated in Table 1. The photostationary state was achieved within a minute in acetone solution at room temperature. The *N*-substituent affected both the absorption maxima (λ_{max}) of the colored forms and their half-lives ($t_{1/2}$) for thermal bleaching. Especially, **1b** having an isopropyl group has a 4-fold increase of the half-life of the colored form compared with **1a**. Thermal bleaching was presumably suppressed by the steric hindrance around the spiro carbon. Absorption maxima of the colored form were obviously affected by the solvent polarity: those in acetone being shifted toward longer wavelength by 71-85 nm than those in methanol. Additionally, the colored form of **1** appeared to be more stable in methanol than that in acetone.

The colored forms of spiroindolinobenzothiopyran derivatives were proposed to be the zwitterionic type **9** based on kinetic study[2] or as the thione type **10** by analysis of electron absorption spectra of the colored form



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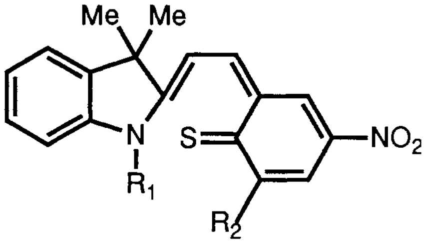

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frozen in a rigid matrix.[1)] The theoretical calculation using INDO/S-CI method[8)] demonstrated that the colored forms of spiroindolinobenzopyrans are in favor of zwitterionic structure, while those of spironaphthooxazines are most likely for keto type. The possible structure for the colored form of **1** was characterized on the basis of data from a ^1H NMR spectroscopy at low temperature in conjunction with a ^1H-^1H homonuclear shift-correlated 2-D NMR technique. Irradiation of **1a** in acetone-d_6 or methanol-d_4 by UV light (365 nm) at -78 °C led to the green color whose NMR spectrum (-40 °C) gave a new single peak at 4.27 ppm which is assignable to the quaternary N^+-CH_3 group of the colored form **9**.[9)] This fact is consistent with the low field shift of the quaternary N^+-CH_3 of 1,2,3,3-tetramethylindolenium iodide (**7**, 4.2 ppm), while the tertiary N-CH_3 protons of **8** appears at 2.9 ppm. The peak intensity at 4.26 ppm decreased at 0 °C with the simultaneous bleaching of the green color. Theoretical calculations by PPP-CI[10)] method for the zwitterionic colored forms suggests that s-trans, s-cis-conformation **11** is the most plausible structure.

When a hexane solution of **1a** was irradiated by UV light (365 nm), light orange crystalline precipitate **12** was obtained in 55% yield from the resulting yellow solution.[11)] Of particular interest is that rapid and drastic coloration to deep green took place *without irradiation* when the precipitate was dissolved in acetone or methanol. Electron absorption spectrum of the resulting colored solution was identical to that of the colored species obtained from **1a** in acetone or methanol upon irradiation. It should be noted that the colored solution of **12** thermally bleached in a minute at 30 °C and the resulting light yellow solution gave the identical NMR spectrum of the spiro form **1a**. Although no significant spectral differences of **12** from **1a** in IR (KBr) and MS analyses were observed,[11)] we thought it most likely the photoprecipitate **12** was related to an

Table 1. The photochromic properties of spiroindolinobenzothiopyrans in methanol and acetone solution at 27.0 ± 1.5 °C

	In methanol solution		In acetone solution	
	λ_{max} nm	$t_{1/2}$ min	λ_{max} nm	$t_{1/2}$ min
1a	588	0.2	673	0.1
1b	581	0.8	652	0.5
1c	590	0.6	662	0.2
1d	590	0.6	660	0.6

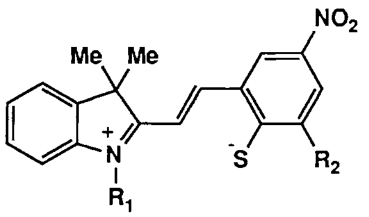

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Fig. 1. s-trans, s-cis-Conformation of the zwitterionic colored form.

intermolecular stacked-crystal[12)] among the spiro form and the colored form, or a cisoid ring open compound **9** as in the case of spiroindolinobenzopyran.[13)] Further structural investigations on **12** and photochromic properties of **1** are now in progress.

The authors are grateful to Professor Sumio Tokita for helpful discussion.

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3) **4**: Brown tar, 90% yield; ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.0 (m, C=C-CH_3, 3H), 3.5 (s, N-CH_3, 6H), 5.3 (s, 3-CH_2, 2H), 5.7 (m, CH_2=C, 1H), 6.2 (m, CH_2=C, 1H), 8.6 (d, aromatic, J=3 Hz), 8.7 (d, aromatic, J=3 Hz), 10.0 (s, CHO, 1H).
4) **5**: Light yellow crystal, 60% yield; mp 93-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, C=C-CH_3, 3H), 3.03 (s, N-CH_3, 3H), 3.22 (s, N-CH_3, 3H), 5.47 (s, 3-CH_2, 2H), 5.68 (s, CH_2=C, 3H), 6.22 (s, CH_2=C, 1H), 8.55 (d, aromatic, J=2.8 Hz, 1H), 8.77 (d, aromatic, J=2.6 Hz, 1H), 10.39 (s, CHO,1H).
5) J. Miyazaki and E. Ando, Japan Patent 62-146978, 1987.
6) **6**: Light yellow powder, 80% yield; ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.0 (s, C=C-CH_3, 3H), 5.3 (s, 3-CH_2, 2H), 5.7 (m, CH_2=C, 1H), 6.2 (m, CH_2=C, 1H), 8.2 (br, SH, 1H), 8.4 (d, aromatic, J=2 Hz, 1H), 8.5 (d, aromatic, J=2 Hz, 1H), 10.0 (s, CHO, 1H).
7) Spectroscopic data for **1a** were typically given as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 3-CH_3, 3H), 1.39 (s, 3-CH_3, 3H), 1.96 (s, C=C-CH_3, 3H), 2.68 (s, N-CH_3, 3H), 5.17 (d, 8'-CH_2, J=14 Hz, 1H), 5.24 (d, 8'-CH_2, J=14 Hz, 1H), 5.61 (s, CH_2=C, 1H), 6.05 (d, 3'-CH, J=11 Hz, 1H), 6.17 (s, CH_2=C, 1H), 6.51 (d, 7-CH, J=7.7 Hz, 1H), 6.67 (t, 5-CH, J=7.5 Hz, 1H), 6.97 (d,4'-CH, J=11 Hz, 1H), 7.07 (d, 4-CH, J=7.7 Hz, 1H), 7.17 (t, 6-CH, J=7.5 Hz, 1H), 8.02 (d, 5'-CH, J=2.3 Hz, 1H), 8.09 (d, 7'-CH, J=2.3 Hz, 1H); IR (cm^{-1}, CCl_4) 3033 (w, $\nu_{\mathrm{s.aromatic\text{-}CH}}$), 2964 (m, $\nu_{\mathrm{asym.aliphatic\text{-}CH}}$), 2868 (w, $\nu_{\mathrm{s.aliphatic\text{-}CH}}$), 1729 (s, $\nu_{\mathrm{C=O}}$), 1607 (m, benzene), 1524 (s, $\nu_{\mathrm{asym.NO_2}}$), 1463 (m, benzene), 1340 (vs, $\nu_{\mathrm{s.NO_2}}$), 1151 (s, $\nu_{\mathrm{asym.ester}}$), 1067 (m, $\nu_{\mathrm{s.ester}}$); MS (EI, 70 eV) m/z= 436 (M^+); mp (DSC) 111-116 °C.
8) S. Nakamura, 24th Symp. Yuuki Electronics Zairyou Kenkyuukai, Preprints p.7, 1988.
9) ^{1}H NMR (-40 °C, acetone-d_6) δ 1.20 (s, 3-CH_3, 6H), 1.87 (s, C=C-CH_3, 3H), 4.27 (s, N-CH_3, 3H), 5.81 (s, CH_2=C, 1H), 6.07 (s, CH_2=C, 1H), 7.6-7.7 (m, 2H), 7.8-8.0 (m, 3H).
10) A. Miyashita, M. Hirano, S. Tokita, and H. Nohira, unpublished results.
11) **12**: IR (cm^{-1}, KBr) 2961 (w, $\nu_{\mathrm{s.aliphatic\text{-}CH}}$), 1726 (s, $\nu_{\mathrm{C=O}}$), 1637 (m, vinyl), 1606 (m, benzene), 1518 (s, $\nu_{\mathrm{asym.NO_2}}$); MS (EI, 20 eV) m/z= 436 (M^+); mp (DSC) 109-118 °C.
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(Received October 15, 1990)