Negative Photochromism of 3, 1'-Trimethylene-Bridged 6-Nitroindolinospiropyran

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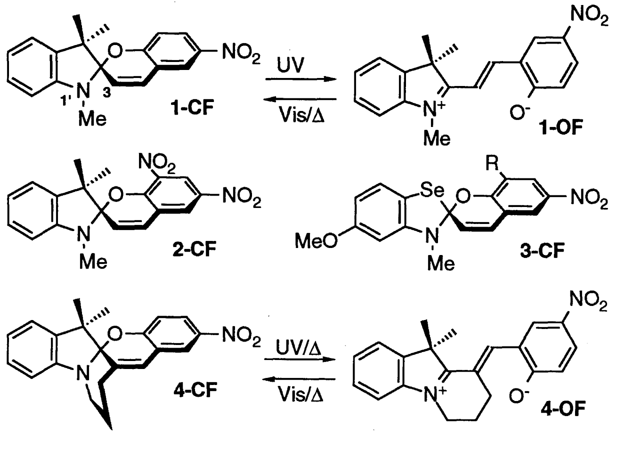
(Received September 26, 1994)

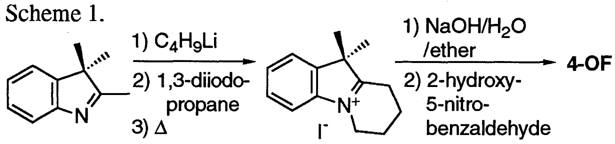
A new photochromic nitroindolinospiropyran with a 3,1'-trimethylene bridge was synthesized. Different from the non-bridged spiropyrans it exists mainly as the colored twitter-ionic open form in polar solvents. The following values in $CHCl_3$, DMSO, and CH_3OH at 20 °C were determined: (1) molar absorption coefficient of the open form at λ_{max}, (2) Arrhenius' activation energy, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ of thermal coloring and bleaching, (3) ΔG, ΔH, and ΔS of the thermal coloring.

Spiropyrans are the best studied photochromic compounds,[1] and several attempts to apply them to the construction of photofunctional molecules have been reported recently.[2] The most remarkable feature of spiropyrans like commercially available **1** is the thermal reversibility of the colored open form (OF) generated by UV-light irradiation to the colorless closed form (CF). To the contrast, some of the examples found in the early literature[3] (**2**) through recent studies[4] (**3**) revealed that a certain stabilization appended to the open form allowed the spiropyran derivatives to exist as the thermal equilibrium mixture of CF and OF.[1b] However, little has been undertaken to give this property to **1** by faint molecular modifications. Furthermore, determination of the value of molar absorption coefficient of the open form of **1** and the derivatives is difficult.[1b] If a simple, electronically less influential modification of **1** would make OF exist stably, it should give important information about the molar absorption coefficient of OF of **1**. We here report that an alkyl-chain-bridged spiropyran **4** exists as the equilibrium mixture of CF and OF in polar solvents.

Synthesis of the new spiropyran **4**, obtained as amorphous purple solid[5] in 53% overall yield, was carried out as shown in Scheme 1.



Scheme 1.



Spiropyran **4** was dissolved in 13 different solvents listed in the increasing order of $E_T(30)$[6] in Table 1. Although **1** is colorless in these solvents, **4** was strongly colored in some polar solvents (dimethyl sulfoxide (DMSO), acetonitrile, 2-propanol, acetic acid, ethanol, and methanol). While irradiation of visible light to the solution of **4** in these solvents vanished the color, it recovered gradually towards the initial absorbance when the irradiation was stopped. These facts imply that **4** exhibits the negative photochromism in polar solvents. Absorption spectrum of **4** in methanol at 293 K at the thermal equilibrium is depicted in Figure 1. Obviously the alkyl chain in **4** appended certain destabilization caused by sterical strain to CF.[7] As little differences in the degree of strain in planar OFs of **1** and **4** are expected, ΔG of coloration from **4-CF** to **4-OF** must be quite small. In some polar solvents, it becomes negative.

Table 1. Absorption spectroscopic properties of spiropyran **4**[a]

Solvents	λ_{max} / nm	Absorbance at λ_{max}
Toluene	630	1.5×10^{-3}
Tetrahydrofuran	607	9.7×10^{-3}
Ethyl acetate	606	9.3×10^{-3}
Chloroform	598	74.8×10^{-3}
Pyridine	599	99.4×10^{-3}
Dichloromethane	590	94.5×10^{-3}
Acetone	584	85.5×10^{-3}
Dimethyl sulfoxide	572	65.1×10^{-2}
Acetonitrile	573	24.5×10^{-2}
2-Propanol	547	37.4×10^{-2}
Acetic acid	*391*	90.2×10^{-2}
Ethanol	529	70.1×10^{-2}
Methanol	517	64.4×10^{-2}

[a] Concentration of **4**: 6.24×10^{-5} mol dm^{-3} for all the solvents used. Temperature: 293 K.

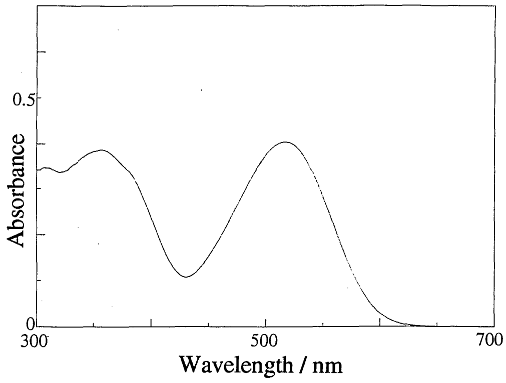


Figure 1. Absorption spectrum of **4** in methanol.
4: 4.12×10^{-5} mol dm^{-3} (293 K).

Table 2. K_{eq}s, ΔGs of coloring reaction, coloring and bleaching reaction rate constants, and ε_{max} of **4** at 293 K.

Solvents	K_{eq}	ΔG / kJ mol^{-1}	k_c / 10^{-3} s^{-1}	k_b / 10^{-3} s^{-1}	$\varepsilon_{max}{}^{a}$ (λ_{max} / nm)
Chloroform	0.039	7.9	8.6	2.2×10^2	3.2×10^4 (598)
Dimethyl sulfoxide	0.60	1.2	3.7	6.0	2.8×10^4 (572)
Methanol	5.7	-4.2	6.9	1.2	1.2×10^4 (517)

^{a} ε_{max} / mol^{-1} dm^3 cm^{-1}.

Table 3. Kinetic parameters of thermal coloring reaction of **4** at 293 K.

Solvents	E_a / kJ mol^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ / kJ mol^{-1}
Chloroform	90 ± 12	88 ± 12	14 ± 42	84 ± 0
Dimethyl sulfoxide	78 ± 2	75 ± 2	-35 ± 7	86 ± 4
Methanol	83 ± 2	81 ± 2	-11 ± 6	84 ± 4

Table 4. Kinetic parameters of thermal bleaching reaction of **4** at 293 K.

Solvents	E_a / kJ mol^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ / kJ mol^{-1}
Chloroform	86 ± 2	84 ± 2	29 ± 8	75 ± 0
Dimethyl sulfoxide	84 ± 2	81 ± 2	-10 ± 7	84 ± 4
Methanol	66 ± 9	63 ± 9	-84 ± 33	88 ± 19

As shown in Table 1, λ_{max} of OF shortened as the solvent polarity increased. This is in good accordance with the previous finding[1b,8] that OF of spiropyrans are rather twitter-ionic than neutral merocyanine-like. The only one exception is acetic acid. We assume that the phenoxide anion of OF was protonated in acetic acid, for λ_{max} of OF of **1** also shortened in acetic acid (531 nm in ethanol to *ca.* 410 nm (shoulder) in acetic acid). As the equilibrium constant K_{eq} ($=k_c/k_b$, where k_c is the rate constant of coloration, and k_b is that of bleaching) depends on solvent polarity (*vide infra*), the absorbance changes significantly.

The equilibrium constants K_{eq} between **4-CF** and **4-OF** at 293 K in chloroform, DMSO, and methanol were calculated from the concentration ratio of them determined by ^{1}H NMR in the corresponding deuterated solvents, from which the molar absorption coefficients of **4-OF** at λ_{max} of visible light region and the change in free energy (ΔG) of the coloring reaction (**4-CF** to **4-OF**) in these solvents were calculated. These data at 293 K, together with k_c and k_b obtained from K_{eq} and the Guggenheim method[9] applied to the thermal coloring or bleaching reactions of **4**, are shown in Table 2.

Keq, k_c, and k_b at various temperatures in these solvents were also determined by the Guggenheim method. Arrhenius plots of k_c and k_b gave the Arrhenius' activation energy (E_a), activation enthalpy ($\Delta H^{\ddagger}$), activation entropy ($\Delta S^{\ddagger}$), and activation free energy ($\Delta G^{\ddagger}$) of coloring and bleaching reactions at 293 K. These values are summarized in Tables 3 and 4. Furthermore, ΔG, ΔH, and ΔS from **4-CF** to **4-OF** are calculated from the data in Tables 3 and 4, and listed in Table 5.

Table 5. Thermodynamic parameters of the reaction from **4-CF** to **4-OF** at 293 K.

Solvents	ΔH^a	ΔS^b	ΔG^a
Chloroform	4 ± 10	-15 ± 34	8 ± 0
Dimethyl sulfoxide	-6 ± 0	-25 ± 0	2 ± 0
Methanol	18 ± 7	73 ± 27	-4 ± 15

^{a} ΔH, ΔG: / kJ mol^{-1}. ^{b} ΔS: / J mol^{-1} K^{-1}.

References and Notes

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5 **4**: amorphous solid; IR (KBr) 1606, 1518, 1484, 1454, 1339, 1261, 744 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.22, 1.31 (each 3H, s), 1.75 (2H, m), 2.11 (1H, m), 2.39 (1H, m), 3.47 (1H, m), 3.65 (1H, m), 6.50 (1H, s), 6.63 (1H, d, J = 7.9 Hz), 6.81 (1H, dd, J = 7.3, 7.6 Hz), 6.94 (1H, d, J = 8.9 Hz), 6.97 (1H, d, J = 7.6 Hz), 7.16 (1H, t, J = 7.6 Hz), 7.95 (1H, s), 8.04 (1H, d, J = 8.9 *Hz*).

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7 A nitroindolinospiropyran with a tetramethylene-bridge did not show negative photochromism in any solvents.

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