January, 1990] © *1990 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *63*, *267—268 (1990)* 267

A New Photochromic Spiro[3*H*-1,4-oxazine]

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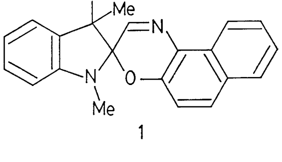
(Received April 4, 1989)

Synopsis. A new photochromic spiro[3*H*-1,4-oxazine] **4** is described. The absorption spectra of **4** have been examined and compared with those of spiro[indoline-naphthoxazine] **1**. The colored form of **4** has the absorption maximum shorter than that of **1**. Compound **4** showed excellent light fatigue-resistant property.

A photochromic compound is characterized by its ability to undergo a reversible color change between two forms, which is induced in at least one direction by the absorption of light. Although the photochromic compounds have long been attracting significant attention because of their potential ability for sunlight-activated self-darkening glasses as well as for optical memory media, they still await major commercial exploitation. The reasons for this are the lack of a fatigue-resistant property to light and color variations. Recently, it has been reported that spiro[indoline-naphthoxazine] **1** has excellent fatigue-resistant property to light, and it takes longer than 200 h in actual use to lose half of its photocolorability.[1,2] **1** has a 3*H*-1,4-oxazine ring instead of a 2*H*-pyran ring of spiro[benzopyran-indoline] **2**.[3] The fatigue-resistant property is considered due to photochemical stability of the oxazine molecular framework in the ring-closed form as well as in the open-ring form. From the view point to get color variations, it is interesting to synthesize a photochromic spiropiperidine derivative **4** which has an oxazine ring instead of a 2*H*-pyran ring of spiro[benzopyran-piperidine] **3**.[4,5] The compound is expected to have a fatigue-free property and the absorption maximum shorter than that of compound **1**.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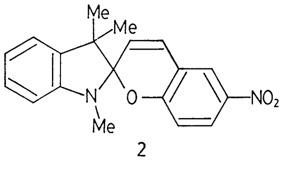
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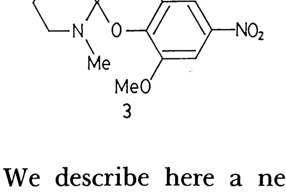
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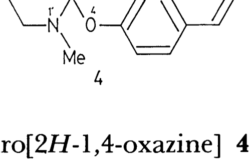

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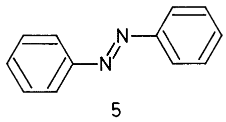
We describe here a new spiro[2*H*-1,4-oxazine] **4**, which shows a reversible photochemical color change from colorless to pink in methanol solution at room temperature. The light fatigue resistance has also been examined and compared with those of typical photochromic compounds, **1**, **2**, azobenzene **5**,[3] and fulgide **6**.[6]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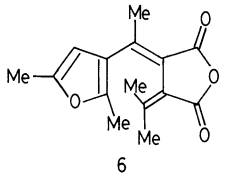
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Experimental

General. IR spectra were measured with a Diglab FTS 15E/D spectrometer. ^{1}H NMR (199.5 MHz) and ^{13}C NMR (50.1 MHz) were measured with a JEOL FX-200 spectrometer in $CDCl_3$. Absorption spectra were measured with a Photal MCPD-1000. A Hamamatsu 100 W Hg-Xe lamp was used as the light source. In the fatigue-resistant property measured, a Lambda Physik EMG-50E XeCl excimer laser and an Osram 450 W Xe lamp were used.

Synthesis of 1′,3′,3′-Trimethylspiro[3*H*-naphth[2,1-*b*][1,4]-oxazine-3,2′-piperidine] (4). 1-Nitroso-2-naphthol (6.93 g) was added to ethanol (70 ml), and the mixture was heated under reflux to completely dissolve 1-nitroso-2-naphthol under nitrogen atmosphere. To the solution, a slurry of 1,2,3,3-tetramethyl-3,4,5,6-tetrahydropyridinium iodide[7] (10.7 g), triethylamine (11.2 ml), and ethanol (40 ml) were added and refluxed for 2 h. The reaction mixture was allowed to stand for a few days and the brown precipitate was obtained by filtration. The precipitate was recrystallized from ethanol or methanol to give pale yellow needles **4** (a few-10%): mp 104—105 °C; ^{1}H NMR ($CDCl_3$) $\delta=0.98$ and 1.26 (6H, s, 3′-Me), 2.23 (3H, s, N-Me), 1.29—2.94 (6H, m, 4′-, 5′-, 6′-H), 7.05—8.52 (7H, m, aromatic H); ^{13}C NMR ($CDCl_3$) $\delta=20.9$ (5′-C), 22.0 and 26.4 (3′-Me), 32.8 (4′-C), 39.5 (N-Me), 39.9 (3′-C), 48.2 (6′-C), 92.6 (spiro-C), 116.6 (5-C), 121.4 (10-C), 122.3 (10b-C), 123.6 (8-C), 126.8 (9-C), 127.6 (7-C), 128.9 (6a-C), 129.8 (6-C), 131.1 (10a-C), 145.6 (4a-C), 153.0 (2-C). Found: C, 77.79; H, 7.53; N, 9.64%. Calcd for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52%.

Results and Discussion

A 2.7×10^{-5} mol dm^{-3} methanol solution of **4** at 25 °C is colorless and shows three absorption bands in the ultraviolet region. The first two bands in the region from 380 nm to 280 nm have low ε values ($\log\varepsilon=3.72$ at 316 nm). The absorption band in the deep-ultraviolet region has an intense peak at 234 nm ($\log\varepsilon=4.72$).

In analogy with spiropyrans, the two chromophores within spiro[3*H*-1,4-oxazine] **1** and **4** are topologically orthogonal. Thus, the absorption spectrum consists of localized transitions belonging to the particular chromophores of the molecule. Chu has assigned the absorption peaks of **1** at 235 nm and 203 nm to the

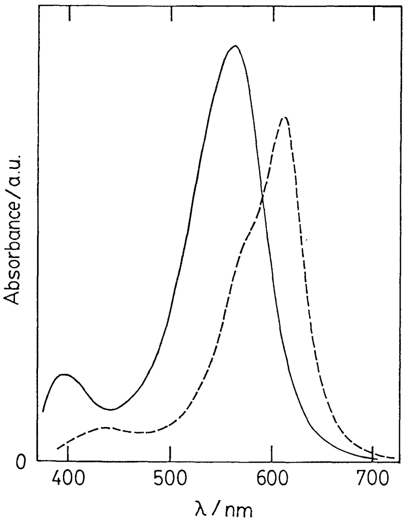

Fig. 1. Absorption spectra of **4** (——), and **1** (----) in methanol at 25 °C after ultraviolet irradiation. Concentrations of **4** and **1** were 2×10^{-4} mol dm^{-3}.

transitions of the indoline chromophore, the peaks at 345 nm and 317 nm to the transitions of the oxazine chromophore, and the peak at 297 nm to the transitions of both oxazine and indoline chromophores.[8] The absorption spectrum of **4** resembles that of **1**, though **4** has an additional peak at 365 nm. *N*-Methylpiperidine has only one weak absorption peak at 213 nm (log ε=3.20) in the ultraviolet region.[9] This suggests that the bands at 365 nm, 234 nm, and 200 nm are all assigned due to the naphthoxazine ring in the compound **4**.

A multichannel diode array photodetector was used to measure the absorption spectrum of the colored form. The photodetector can measure the whole spectrum between 220 nm and 800 nm within 50 ms. A 2×10^{-4} mol dm^{-3} methanol solution of **4** was irradiated with a 100 W Hg-Xe lamp by using a glass filter (HOYA U-360, 400 nm$>\lambda>$300 nm) for a period of 5 min. The visible absorption spectrum of the colored form of **4** is shown in Fig. 1. The visible absorption spectrum of the colored form of **4** has the maximum at 562 nm which is shorter than that of **1** (610 nm). The spectral shape is also different. A shoulder is observed for **1** at the shorter wavelength, but it is not detected for **4**.

Relative light fatigue resistance of **4** was compared with typical photochromic compounds using a XeCl excimer laser (308 nm, 60 mJ/pulse) as the exciting light source and 450 W Xe lamp as the bleaching light source. The colored forms of **5** and **6** were bleached by the light passed through a glass filter (Toshiba VY-45, $\lambda>$450 nm). Absorbance of all compounds at 308 nm before laser flash was adjusted to 0.26. The absorbance at visible absorption maxima for a colored compound after *N* times flashes, A_N, was measured. Relative fatigue curves, A_N/A_1 vs. number of flashes, are shown in Fig. 2. Compounds **4** and **1** have excellent fatigue-resistant property to light in comparison with **2**. The light fatigue resistance of **4** is same as that of **1** up to about 1000 flashes.

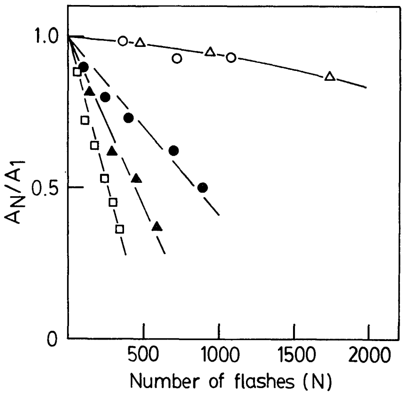

Fig. 2. Relative light fatigue resistance of photochromic compounds: ○, **4** in 2-propanol; △, **1** in 2-propanol; □, **2** in toluene; ●, **5** in toluene; ▲, and **6** in toluene at 25 °C.

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