

## Synthesis of Long-Chain Spirobenzopyrans Bearing a Monoazacrown ether

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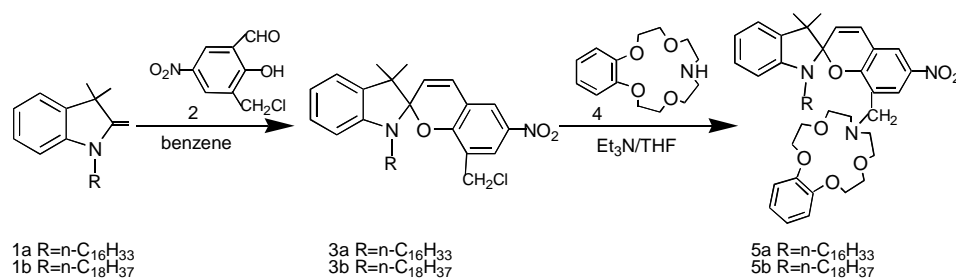
**Abstract:** Two new long-chain spirobenzopyrans and their crowned derivatives were designed and synthesized.

**Keywords:** Synthesis, long-chain, spirobenzopyran, monoazacrown ether.

The photochromic pigments in the chloroplast and in the photoreceptor cell of the vision system have a monolayer organization<sup>1</sup>. It is known that the monolayer assemblies favour the energetic transformations. For the vision process, light-induced isomerization of retinal linked to opsin triggers a conformational change of the protein, of which information is eventually transmitted to the nervous systems by use of messenger molecules<sup>2</sup>.

M. Inouye *et al.*<sup>3</sup>, K. Kimura *et al.*<sup>4</sup> and we<sup>5</sup> independently synthesized spirobenzopyran derivatives incorporating a crown ether moiety which isomerize to their corresponding merocyanine forms to some extent even in the dark when their crown moieties bind alkali metal ions. The isomerization of crowned spirobenzopyrans is induced by recognition of cations as well as by UV irradiation.

In order to study photochromic and cation-induced photochromic properties in monolayers, we designed long-chain spirobenzopyrans bearing a monoazacrown ether, and wish that the aliphatic long-chain forms a monolayer and the crown ether moiety binds alkali metal ions to induce the isomerization of spirobenzopyrans. As preliminary work we present their syntheses in this paper.



Compound **1a**<sup>1</sup>, **1b**<sup>1</sup>, **2**<sup>6</sup>, **4**<sup>7</sup> were prepared according to literature procedures.

Compound **3a** and **3b** (Exemplified with **3a**) : A benzene solution of **1a** and 3-chloromethyl-5-nitrosalicylaldehyde was refluxed for 6h. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel; eluent, AcOEt : petroleum ether=1:10) to give **3a**.

Compound **5a** and **5b** (Exemplified with **5a**) : A THF solution of monoazabenz[15-C-5], compound **3a** and Et<sub>3</sub>N was refluxed for 40h. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel; eluent, AcOEt: petroleum ether=1:10 and 1:3 in turn) to give **5a**.

Spirobenzopyran **5a** and **5b** show negative photochromism, that is, they give in the dark moderately coloured forms that are reversibly bleached with UV light, and Li and Na ion can induce the isomerization of **5a** and **5b**. Their photochromic properties in monolayers are under study.

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#### References and Notes

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8. Spirobenzopyran **3a**: Yield 37%; oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90MHz) δ 0.88 (3H, t) ; 1.22 (34H, m) ; 3.08 (2H, t) ; 4.32 (2H, s) ; 5.85 (1H, d) ; 6.50 (1H, d) ; 6.75-7.10 (4H, m) ; 7.90 (1H, d) ; 8.10 (1H, d) . IR (neat) 2924; 2853; 1610; 1524; 1457; 1339; 1281; 1094; 918; 744cm<sup>-1</sup>. FABMS (in 3-nitrobenzyl alcohol) m/e (rel intensity) 582 (MH<sup>+</sup>, 35) ; 545 (M<sup>+</sup>-Cl, 35) . Anal. Calcd for C<sub>35</sub>H<sub>49</sub>N<sub>2</sub>O<sub>3</sub>Cl: C, 72.35; H, 8.44; N, 4.82. Found: C, 72.05; H, 8.38; N, 4.87. Spirobenzopyran **5a**: Yield 45%; oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90MHz) δ 0.88 (3H, t) ; 1.22 (34H, m) ; 2.65 (4H, t) ; 3.08 (2H, t) ; 3.40-4.12 (14H, m) ; 5.80 (1H, d) ; 6.50 (1H, d) ; 6.75-7.10 (8H, m) ; 7.90 (1H, d) ; 8.10 (1H, d) . IR (neat) 2924; 2853; 1608; 1521; 1454; 1334; 1258; 1130; 933; 742 cm<sup>-1</sup>. FABMS (in 3-nitrobenzyl alcohol) m/e (rel intensity) 813 (MH<sub>2</sub><sup>+</sup>, 10) ; 835 (MH<sup>+</sup>+Na, 5) ; 851 (MH<sup>+</sup>+K, 5) ; 545 (M<sup>+</sup>-crown ether, 65) . Anal. Calcd for C<sub>49</sub>H<sub>69</sub>N<sub>3</sub>O<sub>7</sub>: C, 72.50; H, 8.51; N, 5.18. Found: C, 72.27; H, 8.58; N, 5.12.

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