

## Crowned Spiro-naphthoxazine: Lithium Ion-selective Colouration and Ion-regulated Thermal Stability of its Coloured Form

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A spiro-naphthoxazine derivative incorporating a monoaza-12-crown-4 moiety at the 5'-position has been designed which shows high lithium ion-selective isomerization to the corresponding coloured open form and also lithium ion-concentration dependent thermal stability.

Spirobenzopyran derivatives carrying a crown ether moiety, namely, crowned spirobenzopyrans, are photochromic and show selective cation binding.<sup>1-3</sup> Therefore, they possess great potential for application as a key material for photoresponsive membrane potential,<sup>1</sup> photoinduced ionic-conductivity switching<sup>4</sup> and metal ion spectrophotometry. However, the spirobenzopyran skeleton is generally not very photoresistant, which is a great drawback for applications of crowned spirobenzopyrans. Spiro-naphthoxazine derivatives, on the other hand, are known to possess relatively high durability with respect to photoexcitation, although the thermal stability of their coloured open form is quite low.<sup>5</sup> This prompted us to combine a crown ether moiety with a spiro-naphthoxazine skeleton instead of the spirobenzopyran one, in order to obtain highly-durable photochromic crown compounds. Here we report high Li<sup>+</sup>-selective colouration of a spiro-naphthoxazine derivative bearing a monoaza-12-crown-4 moiety at the 5'-position, **1**, with easy control of the thermal stability of its coloured open form by Li<sup>+</sup> addition.

Crowned spiro-naphthoxazine **1** was synthesized by condensation of 3-(monoaza-12-crown-4)ylmethyl-1-nitroso-2-naphthol with 1,3,3-trimethylindolenine (reflux, 6 h, in ethanol).<sup>†</sup> In acetonitrile solutions of this photochromic compound, hardly any significant isomerization to its coloured open form proceeds without photoirradiation. Addition of an equimolar amount of alkali metal ions to acetonitrile solutions of **1**, however, brought about its isomerization (Fig. 1), mainly owing to the cation-binding ability of its crown moiety. Attention should be paid to a marked Li<sup>+</sup> effect on the

colouration of the crowned spiro-naphthoxazine. Li<sup>+</sup> addition caused extensive isomerization of **1** to its coloured open form. Na<sup>+</sup> gave only a slight colouration of **1**, while K<sup>+</sup> hardly gave any colouration. Such Li<sup>+</sup> selectivity of crowned spiro-naphthoxazine on the colouration is higher than anticipated, judging from the cation-binding selectivity of its crown moiety, monoaza-12-crown-4. This implies that there is stabilization of the coloured open form by intramolecular interaction of the crown-complexed metal ion with the carbonyl oxygen atom, which is similar to that observed for crowned spirobenzopyrans.<sup>3</sup> This intramolecular axial coordination of the carbonyl oxygen atom, as shown in Scheme 1, was suggested by the appearance of two independent peaks in <sup>7</sup>Li NMR spectra of **1**-LiClO<sub>4</sub> acetonitrile solutions in the dark.

Irradiation by UV light (300–400 nm) of acetonitrile solutions of crowned spiro-naphthoxazine **1** promoted its isomerization to the coloured open form with and without alkali metal salts. After turning off the UV light, the coloured open form of **1** smoothly isomerized back to the colourless closed form. First-order rate constants for the thermal colouration of **1** acetonitrile solutions with and without alkali metal perchlorates are summarized in Table 1. The thermal decolouration, although very rapid without any metal salt, was attenuated considerably by equimolar addition of LiClO<sub>4</sub> (Table 1). This again indicates that there is stabilization of the coloured open form of **1** by the strong Li<sup>+</sup> complexation. The thermal stability of the coloured form is about 50 times greater in the presence of Li<sup>+</sup> than without any metal ion. There are

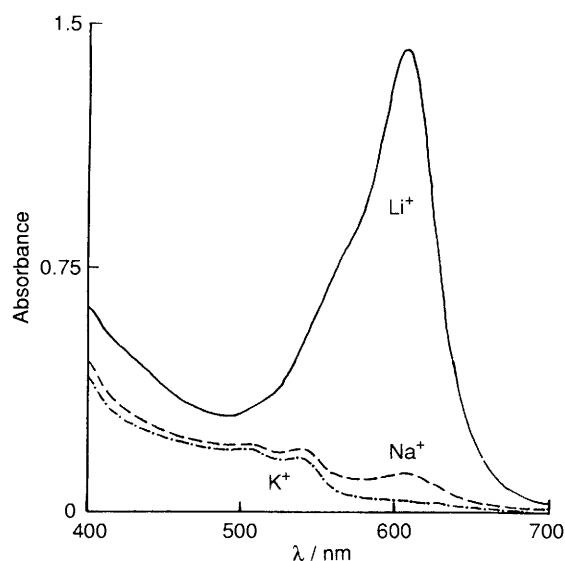
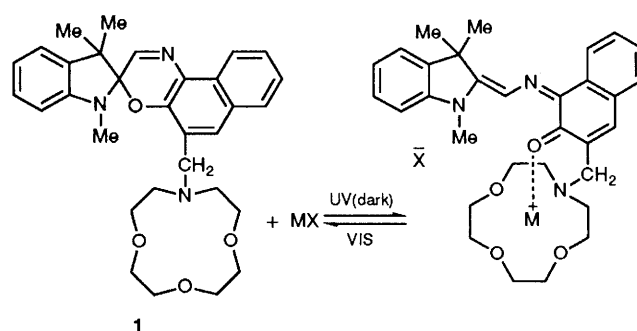


Fig. 1 Absorption spectra of acetonitrile solutions of crowned spiro-naphthoxazine on addition of alkali metal ions under dark conditions. Concentration for **1** and MClO<sub>4</sub>:  $4 \times 10^{-4}$  mol dm<sup>-3</sup> each.



Scheme 1

Table 1 First-order rate constants of thermal decolouration with and without alkali metal ions<sup>a</sup>

Metal ion <sup>b</sup>	Rate constant/ $10^{-3} \text{ s}^{-1}$
None	30
Li <sup>+</sup>	0.59
Li ( $4 \times 10^{-5}$ mol dm <sup>-3</sup> )	2.1
Li ( $4 \times 10^{-6}$ mol dm <sup>-3</sup> )	17
Na <sup>+</sup>	6.0
K <sup>+</sup>	21

<sup>†</sup> Greenish brown glass; *m/z* 516(M<sup>+</sup>); IR,  $\nu_{\text{max}}/\text{cm}^{-1}$  1610 (C=N), 1100 (C–O–C);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.33 (6H, d, *J* 3 Hz, CCH<sub>3</sub>), 2.8–3.0 (7H, m, NCH<sub>2</sub>CH<sub>2</sub> and NCH<sub>3</sub>), 3.6–3.9 (14H, m, OCH<sub>2</sub> and ArCH<sub>2</sub>), 6.5–8.1 (9H, m, aromatic H), 8.67 (1H, d, *J* 8 Hz, N=CH).

<sup>a</sup> Measured in  $4 \times 10^{-4}$  mol dm<sup>-3</sup> **1** acetonitrile solution at 8 °C after 2 min UV-light irradiation. <sup>b</sup> The metal ion concentration is  $4 \times 10^{-4}$  mol dm<sup>-3</sup> unless otherwise stated.

small and almost no addition effect on the thermal stability for Na<sup>+</sup> and K<sup>+</sup>, respectively. It should be also noted that varying Li<sup>+</sup> concentrations can modulate the thermal stability of the coloured open form continuously. This controllable thermal stability of the coloured form is very useful in practical applications of the crowned spironaphthoxazine. Of course, visible light (> 590 nm) caused immediate isomerization back to the colourless closed form even in the presence of Li<sup>+</sup>. So, the photoisomerization of **1** is excellently reversible even in the presence of Li<sup>+</sup>.

Thus, crowned spironaphthoxazine **1** can be isomerized to its coloured open form selectively by Li<sup>+</sup> addition. Also, the thermal stability of the coloured form can be controlled markedly by Li<sup>+</sup> concentration. This compound is, therefore, a promising candidate for a spectrophotometric reagent or

metal indicator of Li<sup>+</sup> as well as for a photoresistant key material for photoinduced switching devices.

*Received, 23rd March 1992; Com. 2/01537D*

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