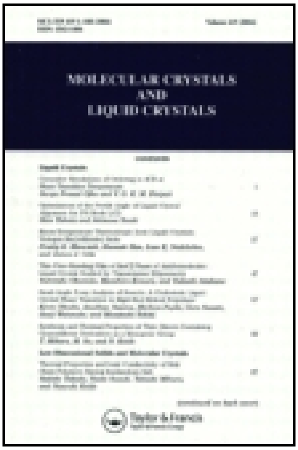

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Photochromic Dispironaphthoxazine Polyethers: Synthesis and Their Cation Binding Capability

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PHOTOCHROMIC DISPIRONAPHTHOXAZINE POLYETHERS : SYNTHESIS AND THEIR CATION BINDING CAPABILITY

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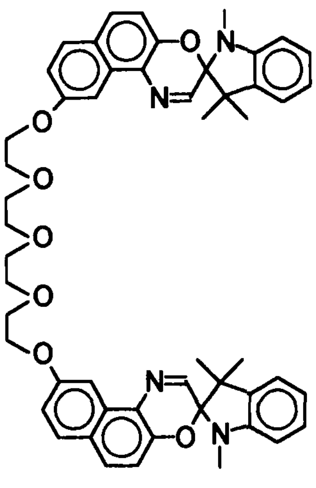
Abstract Dispironaphthoxazines incorporating polyether chain were synthesized. Photochromic effects on cation binding capability of the molecules were investigated. Due to the photochromic spironaphthoxazine unit in these compounds, complexation with metal cations is easily identified by the conventional spectroscopic method. Cation binding ability of dispironaphthoxazine with tetraethylene glycol unit is enhanced under the UV light irradiation. This type of photochromic compound may work as a photoresponsive ionophore.

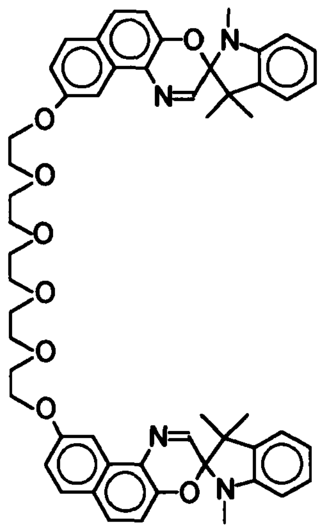
INTRODUCTION

There has been a great interest in organic photochromism not only for the commercial applications but also for the fundamental understanding of photophysical and photochemical processes associated with photochromic behavior. Light filter, binary element for a computer memory, photoswitching, imaging and photography are among the numerous examples of potential application found in photochromic systems. Spirooxazine compounds[1,2] are widely known for their fatigue resistant photochromic properties and have already been commercialized in the field of light filters such as sunglasses. Great efforts are currently being made for both the development of new photochromic materials and advancing the related technology.[3]

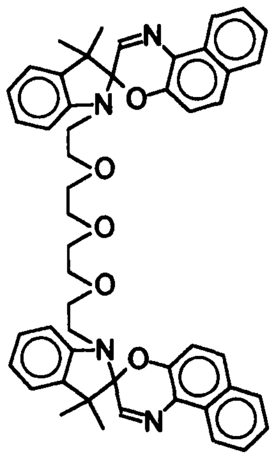
Recently, photochromism was incorporated to the area of molecular recognition, in which a photochromic moiety is linked to a compound bearing recognition site for alkali metal cation such as crown ethers.[4] This type of molecule is particularly interesting for the study of photochromic effect on the recognition ability of a crown ether moiety. Several photochromic dispironaphthoxazine compounds were prepared in this work. Cation binding ability of the spironaphthoxazine moieties linked at oxazine part is compared with the one linked at indoline part. In addition, the effect of polyether chain length on the formation of the recognition site was studied. Preliminary results indicate the cation binding ability changes by the photochromic behavior of the spironaphthoxazine moiety in some dispironaphthoxazine polyethers.



Compound 1



Compound 2



Compound 3

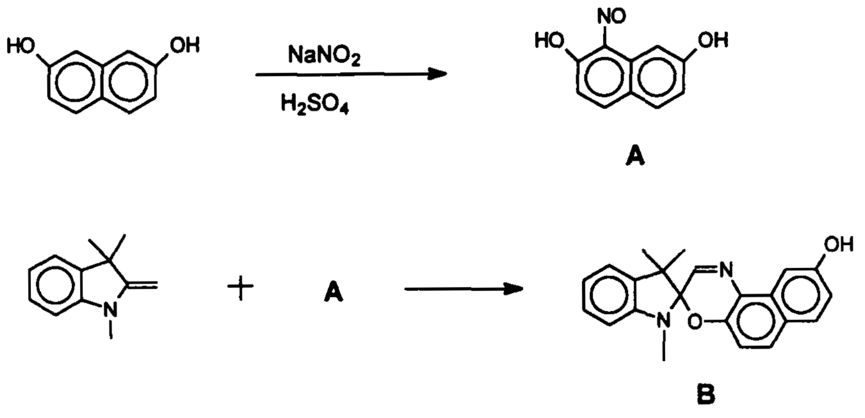
SYNTHESIS

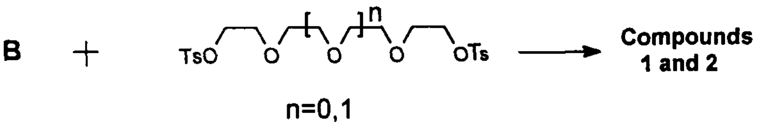
Dispironaphthoxazine polyethers(Compound **1** and **2**) were prepared in three steps as shown in scheme 1. 2,7-Dihydroxy-1-nitrosonaphthalene(A) was synthesized almost quantitatively by nitrosozation of 2,7-dihydroxynaphtalene in the first step. 1,3,3-trimethyl-9′-hydroxyspiro [indoline-naphthoxazine](**B**) is obtained by condensation reaction in the following step.[5] The mixture of 6.0 g (33 mmole) of 2,7-dihydroxy-1-nitrosonaphthalene and 60 ml of absolute ethanol is gently stirred and refluxed, while a solution of 7.2 g(36 mmole) of

2-methylene-1,3,3-trimethylindoline, 5.4 ml of triethylamine and 36 ml of absolute ethanol is added over a 30 minute period. The reaction mixture is refluxed for 2 hours and evaporated under vacuum. The crude product is chromatographed on a silica gel column with dichloromethane as eluent. Recrystallization from ethanol gives 4.2 g(yield 37 %) of compound **B**. In the following step, a solution mixture of 3.5 g (7.7 mmole) of compound **B**, 0.3 g (7.7 mmole) of sodium hydroxide and 3.9 g (7.7 mmole) of tetraethylene glycol ditosylate in 40 ml of anhydrous dichlomethane is stirred at room temperature for 24 hours. The filtrate is washed with water, 5 % acetic acid solution and finally with water again. Recrystallization from acetone gives the final product, compound **1** and **2**. Similar procedure gives compound **3** as shown in scheme 2. Each final product was identified by the proton NMR spectrum. The NMR data for each compound are as follows.

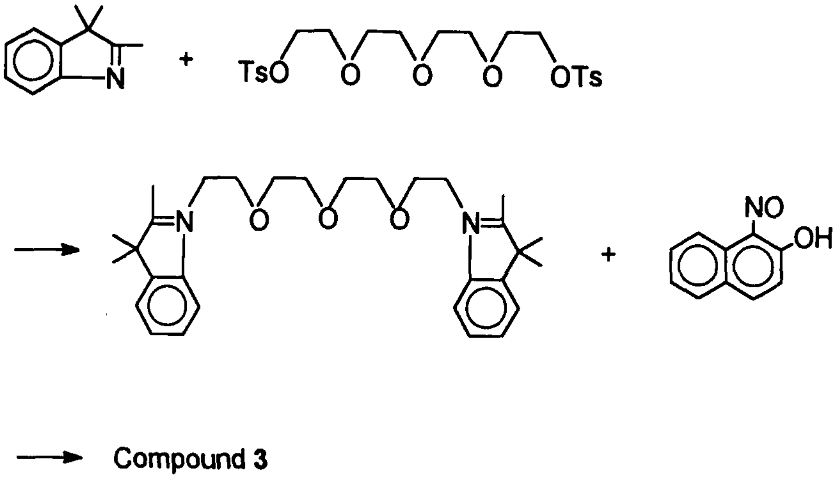
Compound **B** (^{1}H NMR, CDCl$_3$, TMS): δ=1.35 (s, 6, aliphatic), 2.75 (s, 3, tertiary amine), 5.85 (s, 1, hydroxy), 6.5-7.6 (m, 9, aromatic). Compound **1** (^{1}H NMR, CDCl$_3$, TMS): δ=1.35 (s, 12, aliphatic), 2.75 (s, 6, tertiary amine), 3.6-4.5 (m, 20, ethylene glycol), 6.5-7.6 (m, 9, aromatic), 7.88 (s, 1, imine). Compound **2** (^{1}H NMR, CDCl$_3$, TMS): δ=1.35 (s, 12, aliphatic), 2.75 (s, 6, tertiary amine), 3.6-4.5 (m, 16, ethylene glycol), 6.5-7.6 (m, 9, aromatic), 7.88 (s, 1, imine). Compound **3** (^{1}H NMR, CDCl$_3$, TMS): δ=1.32 (s, 12, aliphatic), 3.4-3.7 (m, 16, ethylene glycol), 6.6-7.6 (m, 9, aromatic), 7.7 (s, 1, imine)

Scheme 1





Scheme 2



UV/VIS SPECTRA AND DECAY KINETICS OF THE OPEN FORM

The UV/VIS absorption spectra of closed and open forms of spironaphthoxazine are shown in Figure 1. The spectra were taken for the ethylene glycol solution at −10 °C where the interconversion between the closed and open form occurs very slowly. This is because the viscous media increase the potential barrier for the interconversion between the two forms. The kinetic study shown in Figure 2 also indicates the concentration decay rate of the open form changes enormously in a given temperature range. Interconversion rate is strongly dependent on both the solvent and the temperature. It is difficult to measure the absorption spectra correctly for solutions of low viscosity solvent.

EFFECT OF UV IRRADIATION ON THE RATE OF ION TRANSPORT

To investigate the ion carrying capability of the compounds 1 and 2, experiments were carried out in a U-type cell. A pair of U-type cells

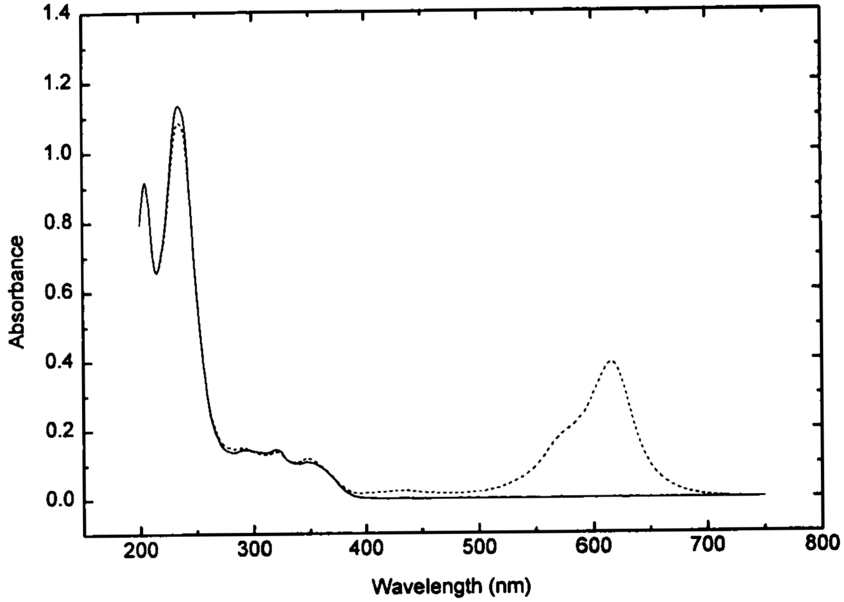


FIGURE 1. Absorption spectrum of spironaphthoxazine in ethylene glycol at −10 °C. The closed form are denoted by solid line and the open form by dashed line.

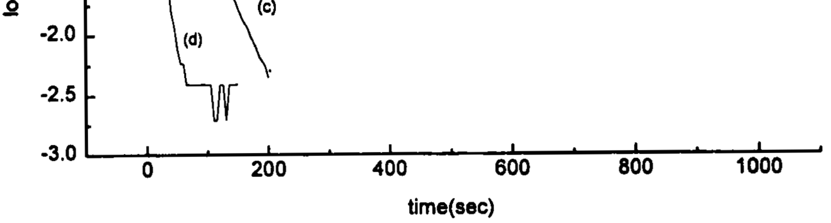


FIGURE 2. Concentration change of the open form of spironaphthoxazine in ethylene glycol as a function of time at different temperatures. (a) −10 °C (b) 0 °C (c) 10 °C (d) 20 °C

was prepared for each compound. One cell was irradiated with 365 nm light and the other cell was left in the dark. The dichloromethane solution of the compounds **1**(compound **2**) was placed in the middle of the U-type cell separating the two acquous phases. Sodium picrate was added to one of the acquous phase and the dichloromethane phase was constantly stirred throughout the measurements. The sodium ion is transported by the carrier molecule from the sodium picrate solution phase to the pure acquous phase with time.[6] The amount of sodium ion transported was measured by the optical density change at the absorption peak of sodium picrate solution. Figure 3 shows the increase of sodium ion concentration transported by the carrier molecules with time. The rate of sodium ion transport increased more in the case of compound **1** when the cell was irradiated with UV. Meanwhile, the UV irradiation has no effect on the transport rate for compound **2**. It is also noted that binding ability of compound **1** for the sodium ion is slightly larger than compound **2**. Some degree of photodegradation was observed for compound **2** which was identified by the electronic absorption tailing in the long wavelength edge. Although the two compounds have different number of recognition sites for the metal cation, the flexible polyether chain would have failed to offer a characteristic configurational environment for the sodium ion complexation. It has been reported that photochromic moiety had no influence on the cation binding ability of the crown ether in the spirooxazine linked crown ether.[4a]

Ion extraction and U-tube experiments were also carried out for compound **3** using Li^+, Na^+ and K^+. The degree of cation extraction was measured by spectrophotometry. It was observed UV irradiation has very little effect on ion extraction rate for compound **3**.

SUMMARY

Photochromic dispironaphthoxazine polyether and its derivatives which would offer different configurations for the cation binding were synthesized. Dispironaphthoxazine with tetraethylene glycol unit showed enhanced sodium ion binding ability under the UV light irradiation while no effect of the UV irradiation was observed for the one with

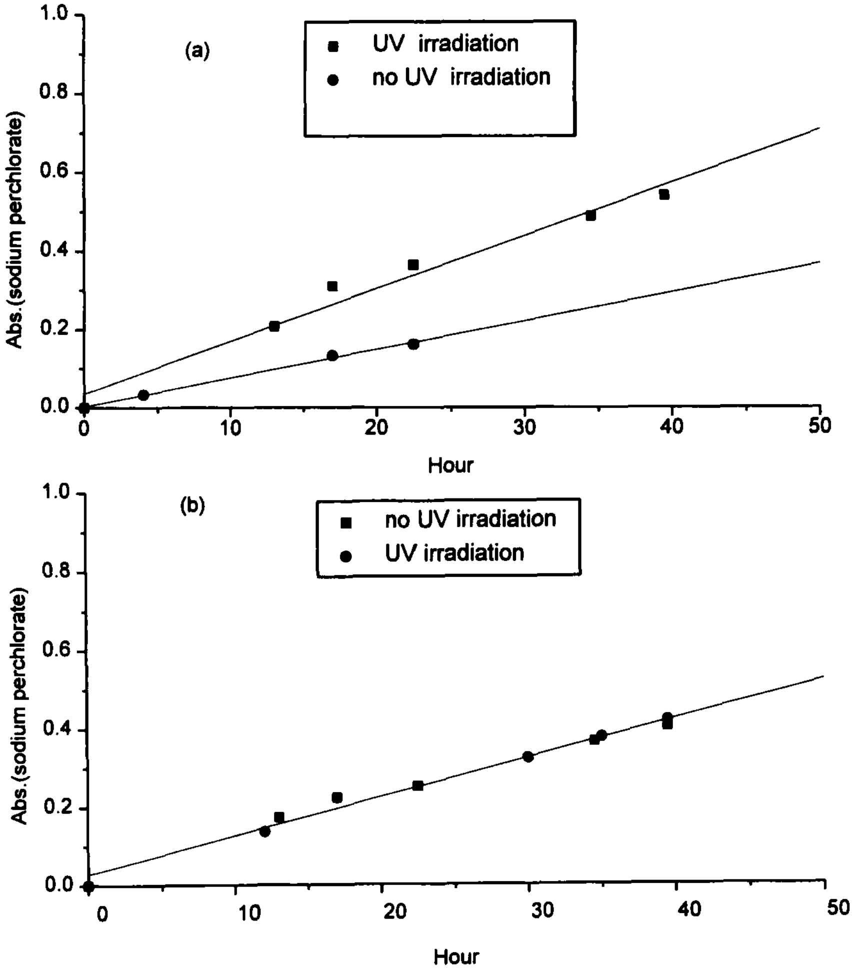


FIGURE 3. Optical density change of sodium picrate solution with time (measured at 380 nm). Points are experimentally measured and lines are the linear least square fit. (a) compound 1/dichloromethane as the ion transport medium (b) compound 2/dichloromethane as the ion transport medium

pentaethylene glycol unit. The selectivity of the sodium ion binding between compounds **1** and **2** is low. This is probably due to the flexibility of polyether chain which reduces any configurational difference between the two compounds. Dispironaphthoxazine polyther in which the nitrogen atom of one indoline part is linked to the other indoline (compound **3**) shows almost no UV irradiation effect. The configuration of the open form of spironaphthoxazine in compound **3** would be less favored than compound **1** or **2** for complex formation. Synthesis of other derivatives with more rigid host system and the complex formation of these compounds with various metal cations are currently under study.

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