

## Synthesis and Selective Coloration of Monoaza Crown Ethers Bearing Picrylamino-type Side Arms for Alkali Metal Salts and Methylamine

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**Abstract:** *N*-pivot lariat ethers with picrylamino group as a chromophore (**1**, **2** and **3**) have been prepared by reaction of *N*-(4-aminoaryl)monoaza crown ethers with picryl chloride, and the selective coloration of **1**, **2** and **3** for alkali metal salts and amines has been studied by UV-Vis spectra.

**Keywords:** Synthesis, selective coloration, monoaza crown ether, alkali metal salts, methylamine.

Host-guest chemistry continues to be an important theme in organic chemistry<sup>1</sup>. As molecular receptors, crown ethers have been widely employed in the field of analytical chemistry, chemical sensors and ionic extraction<sup>2</sup>. Since 4'-picrylamino benzo-15-crown-5 was synthesized by Takagi in 1971, various chromogenic crown ethers have been successively reported<sup>3</sup>, but very limited studies have been reported so far on monoaza-crown ether bearing picrylamino-type side chain<sup>4</sup>. In recent years, many different receptors have been prepared for recognition studies. Such as the receptors containing benzene ring, naphthalene ring, bicyclic guanidium and aza-crown ring. The later can be expected to have some substrate recognition, because the rigid side chain and the aza-crown ring constructed the cleft, which may possess conformational control of N atom<sup>5</sup>. In this paper, we developed *N*-pivot lariat ethers bearing picrylamine group as chromophore (**Scheme 1**) in order to elaborate conveniently the selective coloration of chromogenic crown ether for metal salts and some organic molecules by the UV-Vis spectra.

### Experimental

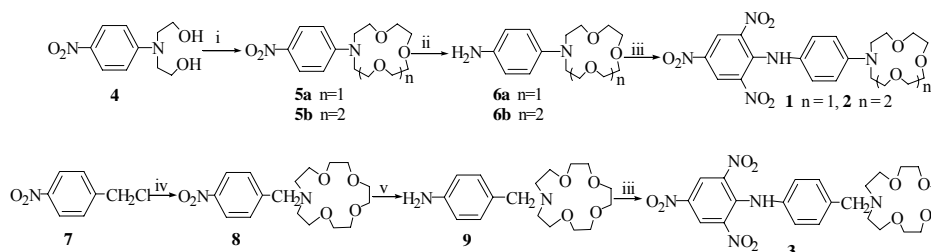
Chromogenic crown ethers **1**, **2** and **3** were synthesized according to the procedure shown in **Scheme 1**. Condensation reaction of 2, 2'-[(4-nitrophenyl) imino] bisethanol **4** with 1.1 eq. of diethyleneglycol ditosylates or triethyleneglycol ditosylates in the presence of NaH and THF to give monoaza crown ethers **5a** (78 %) and **5b**<sup>6</sup> (76 %),

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respectively. Reduction of **5a** or **5b** with Pd/C (10 %) in EtOH at 50 °C provided **6a**<sup>7</sup> (98 %) and **6b**<sup>6</sup> (97 %), respectively; 4-nitrobenzyl chloride **7** was treated with monoaza-15-crown-5 and 2.1 eq. of Na<sub>2</sub>CO<sub>3</sub> in CH<sub>3</sub>CN at reflux to give **8**<sup>8</sup> in 94 % yield. **8** could not reduce with Pd/C to give **9** because the monoaza-15-crown-5 was cleaved from the *N*-(4-nitrobenzyl) monoaza-15-crown-5 by hydrogenation. But **8** could be reduced with 1.3 eq. of SnCl<sub>2</sub>·2H<sub>2</sub>O, conc. HCl and EtOAc to produce **9** (85 %). Finally, the *N*-(4-aminoaryl) monoaza crown ethers (**6a**, **6b** and **9**) were treated with 1.0 eq. of picryl chloride in the presence of Na<sub>2</sub>CO<sub>3</sub> in THF, followed by silica-gel chromatography using CH<sub>3</sub>OH as eluent to provide **1** (67 %), **2** (68 %) and **3**<sup>9</sup> (59 %). The structures of the key intermediates and all the target compounds were determined by <sup>1</sup>H NMR, IR, MS spectra and elemental analysis<sup>9</sup>.

Scheme 1



Reagents and conditions: (i) diethyleneglycol ditosylates or triethyleneglycol ditosylates, NaH, THF, reflux; (ii) H<sub>2</sub>, 10% Pd/C, CH<sub>3</sub>CH<sub>2</sub>OH, 50°C; (iii) Picryl chloride, Na<sub>2</sub>CO<sub>3</sub>, THF, rt; (iv) monoaza-15-crown-5, CH<sub>3</sub>CN, Na<sub>2</sub>CO<sub>3</sub>, reflux; (v) SnCl<sub>2</sub>·2H<sub>2</sub>O, conc. HCl, EtOAc, 40°C.

## Results and Discussion

Absorption maxima of crown ethers **1**, **2** and **3** and their complexes were at visible region. The wave length of the maximum absorption of **3** is far shorter compared to **1** and **2**, due to the methylene bridge between the nitrogen atom of crown ether ring and benzene ring weakened auxochromic role of tertiary amine group. As shown in **Table 1**, crown ether **3** exhibited a moderate selective coloration towards LiCl, but **1** and **2** did not, it is interesting to note that **1** showed selective coloration for LiClO<sub>4</sub>, and the absorption maxima shifted from 118 nm to shorter wave lengths. The interaction of **1** with NaClO<sub>4</sub> and KClO<sub>4</sub> did not induce the changed color. It is likely that compounds **2** and **3** exhibited characteristic performance when they interacted with above alkali metal salts, **2** with NaClO<sub>4</sub> afforded only a slight spectral change. Compound **3** has moderate interaction with LiCl, LiClO<sub>4</sub>, NaClO<sub>4</sub> and KClO<sub>4</sub>. But in all cases the absorption maxima shifted to a longer wave lengths with no selectivity. The differences of UV-Vis spectra may be relative to the rigid of the molecular receptor, the diameter of the crown ether ring and the anion of metal salts.

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**Table 1** Absorption maxima ( $\lambda_{\max}$ , nm) and molar absorptivity values ( $\epsilon$ ) of crown ether-alkali metal ion complexes

Alkali Metal Salts	$\lambda_{\max}$ ( $\epsilon$ , $M^{-1}cm^{-1}$ ) $\Delta\lambda_{\max}$		
	<b>1</b>	<b>2</b>	<b>3</b>
Free	478( $1.0 \times 10^4$ )	479( $0.67 \times 10^4$ )	377( $2.17 \times 10^4$ )
LiCl	478( $0.93 \times 10^4$ ), 0	479( $0.63 \times 10^4$ ), 0	440( $1.28 \times 10^4$ ), 63
LiClO <sub>4</sub>	360( $1.1 \times 10^4$ ), -118	479( $0.66 \times 10^4$ ), 0	448( $1.21 \times 10^4$ ), 71
NaClO <sub>4</sub>	478( $1.0 \times 10^4$ ), 0	482( $0.65 \times 10^4$ ), 3	431( $1.12 \times 10^4$ ), 54
KClO <sub>4</sub>	478( $0.79 \times 10^4$ ), 0	481( $0.67 \times 10^4$ ), 2	431( $0.74 \times 10^4$ ), 54

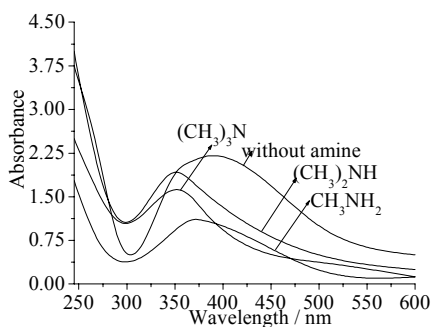
UV-Vis was recorded at  $23 \pm 1^\circ C$  in 1 cm quartz cell by using Hewlett-Packard8452A Diode Array Spectrophotometer. 50%CHCl<sub>3</sub>-50%H<sub>2</sub>O (v : v) was used as the solvent. Concentrations were  $1.0 \times 10^{-5}$  mol/L for crown ethers and  $1.0 \times 10^{-4}$  mol/L for the alkali metal salts and 0.2 mol/L for tetramethyl ammonium hydroxide. Because amino nitrogen atom on crown ether ring may be protonized and affect its coordination with alkali metal ions, to the solution of **1**, **2** and **3** was added tetramethyl ammonium hydroxide, which do not affect the  $\lambda_{\max}$  of chromogenic crown ethers.

**Table 2** Absorption maxima ( $\lambda_{\max}$ , nm) and molar absorptivity values ( $\epsilon$ ) in CHCl<sub>3</sub> of crown ether-organic amine complexes.

Organic amine	$\lambda_{\max}$ ( $\epsilon$ , $M^{-1}cm^{-1}$ ) $\Delta\lambda_{\max}$		
	<b>1</b>	<b>2</b>	<b>3</b>
Free	477( $1.0 \times 10^4$ )	479( $0.67 \times 10^4$ )	377( $2.17 \times 10^4$ )
CH <sub>3</sub> NH <sub>2</sub>	405( $0.67 \times 10^4$ ), -72	478( $0.70 \times 10^4$ ), 0	370( $1.10 \times 10^4$ ), -7
(CH <sub>3</sub> ) <sub>2</sub> NH	477( $1.1 \times 10^4$ ), 0	440( $1.22 \times 10^4$ ), -39	351( $1.92 \times 10^4$ ), -26
(CH <sub>3</sub> ) <sub>3</sub> N	477( $1.1 \times 10^4$ ), 0	457( $1.47 \times 10^4$ ), -22	350( $1.60 \times 10^4$ ), -27
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N	476( $1.1 \times 10^4$ ), 0		

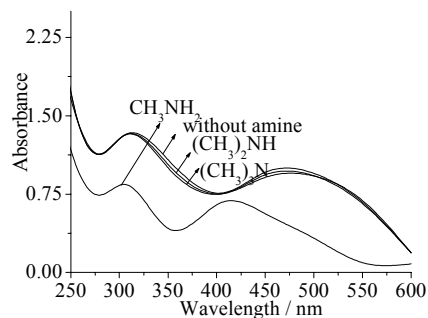
UV-Vis were recorded at  $23 \pm 1^\circ C$  in 1 cm quartz cell by using Hewlett-Packard8452A Diode Array Spectrophotometer. 50%CHCl<sub>3</sub>-50%H<sub>2</sub>O (v : v) was used as the solvent. Concentrations were  $1.0 \times 10^{-5}$  mol/L for crown ethers and  $1.0 \times 10^{-4}$  mol/L for amines

**Figure 1** Absorption spectra of **3** in the absence and presence of amine

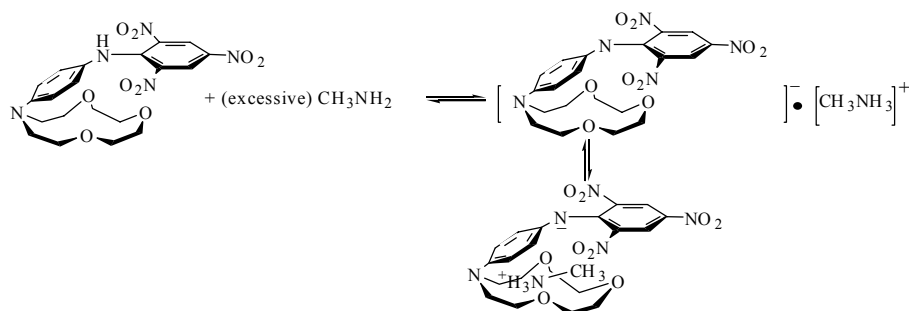


**3** and amine:  $1.0 \times 10^{-5}$  mol/L and  $1.0 \times 10^{-4}$  mol/L, respectively, in CH<sub>3</sub>Cl

**Figure 2** Absorption spectra of **1** in the absence and presence of amine



**1** and amine:  $1.0 \times 10^{-5}$  mol/L and  $1.0 \times 10^{-4}$  mol/L, respectively, in CH<sub>3</sub>Cl

**Figure 3** the possible cleft constructed by the exo-azacrown ether **1**

As shown in **Table 2**, compounds **2** and **3** complexed with  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_3\text{N}$  in certain degree and the  $\lambda_{\text{max}}$  of these complexes shifted to the shorter wavelengths (see **Figure 1**). Compound **1** has a strong coordination towards  $\text{CH}_3\text{NH}_2$  (see **Figure 2**), and its  $\Delta\lambda_{\text{max}}$  is up to 72 nm. The reason might be that  $\text{CH}_3\text{NH}_2$  extracted the hydrogen atom of picrylamino group like triethylamine<sup>3</sup> to form protonated  $\text{CH}_3\text{NH}_3^+$ , the size and shape of  $\text{CH}_3\text{NH}_3^+$  matched well with the cleft (see **Figure 3**) constructed by the exo-azacrown ether **1** and form a more stable intramolecular complexes. The ion pair become more tight with hydrogen bonds, electrostatic forces and vander waals interactions, *et al.*

## References and Note

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