Synthesis, X-ray diffraction and optical spectral study of benzo-18-crown-6 containing monoazo dyes

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The 4′-nitrobenzo-18-crown-6, 2 have been reduced by the Fe/HCl to give 4′-aminobenzo-18-crown-6, 3. This is diazotized and coupled with different phenols to give the corresponding azo-dyes. X-ray diffraction as well as UV-Vis study of 4′ (β-naphthol azo benzo)18-crown-6, 4a dye have been reported.

Keywords: Benzo 18-crown-6, nitration, reduction, diazotization, X-ray, UV-Vis study

Macrocyclic compounds crown ethers are commonly used in phase transfer reactions, biomimetic studies, and selective complexing agents for metals. Recently, crown ether derivatives with ethereal anionic groups on the periphery of the macrocycles have been developed, in order to increase metals electivity and complex stability in analytical and separation methods as well as in biological membranes1-3. Several workers have reported modified crown ethers with chromogenic groups4-6. It is known that varying the size of the crown ether ring or the chromophoric side arm can modify the properties of these compounds. Such changes produce agents with different sensitivities and selectivities for metal ions, including crown ether based dyes possessing a potential anionic site attached to the chromophore7. These structures form intermolecular ion-pair complexes with various metal cations8. Other types of crown ether dyes are those that do not contain ionic groups in the vicinity of the chromophore. Considerable attention has been focused on crown ether dyes containing a chromophore such as picrylamine9 that can be used for photometric determination of alkali and alkaline earth metal ions. Azo dyes such as the p-dimethylaniline-based crown dyes10 have also been employed for complexing alkali and alkaline earth metal ions. The synthesis of crown ether based azo dyes in which an aniline derivative was diazotized and coupled with a phenol residue in a crown ether moiety has also been reported11. Herein is described the syntheses of some novel dyes containing crown ether in different chromophoric environment and their cation complexation behavior by using UV-Vis spectroscopy (Scheme 1).

Results and Discussion

In the ongoing program the synthesis of benzo-18 crown-6 containing mono-azo dyes has been attempted. Benzo-18-crown-6 is nitrated to give 4′-nitrobenzo-18-crown-6, 2 and subsequently reduced by Fe/HCl to get 3 in good yields. Diazotization and coupling with different phenols yielded the corresponding dyes. The structures of synthesized dyes have been established on the basis of IR, 1H and 13C NMR. The synthesized dye 4′-β-naphthol azo-benzo)-18-crown-6 showed good complexion ability with alkaline earth metals like Ca(II) and Ba(II).

Experimental Section

Melting points were recorded in open capillary and are uncorrected. IR spectra were recorded on a Perkin-Elmer FTIR spectrometer using KBr pellets. 1H and 13C NMR (400 MHz) spectra were recorded on a Bruker spectrometer in CDCl3/DMSO-d6 solvent using TMS as internal standard. The UV-Vis spectra were measured using Elico UV-Vis spectrophotometer and X-ray diffraction measurement has been performed on a Philips Analytical XRD spectrometer.

Synthesis of 4′-nitrobenzo-18-crown-6, 2

To 0.612 g (2 mmole) of monobenzo-18-crown-6, 1 dissolved in a mixture of 10 mL of chloroform and 10 mL of acetic acid, 1.7 mL of nitric acid (70%) was added dropwise over a 30 min period. The mixture was stirred for 24 hr at RT and then neutralized with aqueous Na2CO3 and the aqueous layer was extracted with CHCl3, and the combined chloroform extracts were dried over anhyd. MgSO4. After evaporation of CHCl3 a yellow solid was obtained which was purified by recrystallization from ethanol. m.p. 70-72°C, (Lit12: 72°C). Yield 75%. IR (KBr): 3090.71,
Synthesis of 4'-aminobenzo-18-crown-6, 3
To 0.179 g (0.5 mmole) of 4'-nitrobenzo-18-crown-6 in 5 mL ethyl alcohol was added 0.100 g of NH₄Cl and then 1-2 pieces of freshly cut iron. The reaction mixture was refluxed for 3-4 hr. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled to RT. After evaporation of ethyl alcohol, a brown colored solid was obtained. m.p. 54°C. Yield 65%. IR (KBr): 3418.03, 3380, 2920.96, 1623.82, 1516.84, 1456.89, 1354.14, 1283.67, 1184.09, 1119.76, 989.57, 956.66, 835.90 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 3.6-4.4 (m, 20H, -CH₂-), 6.8-8 (m, 3H); ¹³C NMR (300 MHz, CDCl₃): δ 174.50, 154.15, 148.25, 141.34, 117.86, 110.84, 107.57, 70.66, 70.64, 70.54, 70.50, 70.31, 68.88, 68.84, 68.76.

Synthesis of benzo-18 crown-6 diazonium salt of crown ether
The 4'-aminobenzo-18-crown-6 3 (0.25 mmole) were suspended in 3-4 mL of conc. HCl and cooled in an ice-salt mixture to 0-5°C. An aqueous solution of 0.4 g of sodium nitrite in 5 mL water was added slowly and the resulting diazonium chloride was maintained at 5°C. Freshly prepared solution of aryl diazonium salt crown ether of benzo-18 crown-6 was used as such for subsequent coupling reaction.

Synthesis of 4'-β-naphthol azo benzo)-18-crown-6, 4a
A cold aqueous solution (0.25 mmol) of diazonium salt of benzo-18-crown-6 was added dropwise to a solution containing (0.25 mmol) of β naphthol in 5 mL of 10% NaOH and kept stirred at 0°C in an ice bath. A violet red crystalline dye separated out after the addition of diazonium chloride. It was allowed to stand at 0°C for a further period of 30 min and the product, (4'-β- naphthol azo benzo)-18-crown-6, 4a was filtered. m.p. above 300°C. Yield 85%. IR(KBr): 3296.78, 2923.66, 1630.95, 1602.19, 1513.97, 1467.42, 1407.03, 1277.73, 1173.75, 959.30, 844.10, 813.96, 742.16 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 3.65-4.2 (m, 20H, -CH₂-), 6 (bs, 1H, OH) 6.8 -7.8 (m, 9H); ¹³C NMR (300 MHz, CDCl₃): δ 153.64, 147.95, 141.24, 134.60, 129.70, 128.77, 127.71,126.39, 126.28, 123.42, 117.89, 117.78, 110.54, 109.42, 107.23, 70.50, 70.39, 70.19, 68.75, 68.59, 68.42.
(4'-α naphthol azobenzo)-18-crown-6, 4b

An aqueous solution of aryl diazonium salt of amino benzo-18-crown-6 was prepared by above procedure. This aryl diazonium salt of amino benzo-18-crown-6 was gradually added to a cold alkaline solution of α naphthol. After completion of addition, a reddish brown colored dye separated out. It was then allowed to stand at 0°C for a further period of 30 min and the product (4'-α naphthol azobenzo)-18-crown-6, 4b was filtered. m.p. above 300°C. Yield. 75%. IR(KBr): 3400, 2923.94, 1600.22, 1469.89, 1384.41, 117.59 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆): δ 2.5 (bs, 1H, OH) 3.4-4.2 (m, 20H, -CH₂-), 6.8 -7.9, m (9H); ¹³C NMR (300 MHz, CDCl₃): δ 153.57, 134.63, 129.76, 128.82.86, 127.71, 126.42, 126.36, 123.47, 119.74, 77.45, 77.23, 77.02, 76.60.

(4'-8-hydroxy quinoline azobenzo)-18-crown-6, 4c

Yield 67%. m.p. above 300°C. IR(KBr): 3444.22, 2924.67, 1655.14, 1603.44, 1509.32, 1433.80, 1267.15, 1185.90,1134.14, 954.20,705.58 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆): 2.1 (bs, 1H, OH), 3.4-4.2 (m, 20H, -CH₂-), 6.8 (dd, 1, Hb), 7.2 (d, 1, Hc), 7.7 (d, 1, Ha), 7.71-7.89 (m, 4H); ¹³C NMR (300 MHz, CDCl₃): δ 154.14, 152.18, 148.23, 147.85, 141.29, 138.25, 136.10, 128.49, 127.69, 121.77, 117.85, 110.86, 110.05, 107.67, 70.69, 70.52, 70.34, 68.90, 68.85.

Optical Spectral Properties

UV-Vis measurements: Stock solutions of 4a, i.e. (4' β naphthol azobenzo)-18-crown-6 was prepared in ethanol (1 × 10⁻⁴ M) and metal ions such as Cu(II), Fe(II), Ba(II), Ca(II) (1 × 10⁻² M in methanol) were prepared. The metal solutions have been diluted 10 and 100 times to give 1 × 10⁻³ M and 1 × 10⁻⁴ M solutions. Aliquot of metal solution was added to the ionophore solution and the final concentration and composition of the solution were adjusted to the desired value by adding extra ethanol. Out of these four metal ions only Ba(II) and Ca(II) gave the satisfactory results as shown in UV-Vis spectra (Figure 1). It shows a broad absorption band at 322 nm in ethyl alcohol solution, which is a characteristic feature of crown ether dyes moiety, i.e. 4'-(β-naphthol azo benzo)-18-crown-6, 4a. Addition of 100 equivalents of metal ions like Ca(II), Ba(II), Cu(II) and Fe(II) resulted in the formation of metal complex with evolution of heat. In all of these, there is evolution of heat but not in case of Ba²⁺ and Ca²⁺ ions. The colour of the solution changes from red to green and orange in case of copper (II) and iron (II) respectively. The results have been presented in Figure 1.

X-ray diffraction study of 4'-(β-naphthol azo benzo)-18-crown-6, 4a

X-ray scattering measurement was performed on a Philips Analytical XRD spectrometer. The diffractometer type used for the same compound is PW 3710 based. The anode tube used for the same compound is of copper. On the basis of X-ray diffraction spectra peaks observed are very sharp from this it is clear that compound having crystalline nature.

Conclusions

In conclusion, reduction of 4'-nitrobenzo-18-crown-6, 3 by using easily available iron metal, which is very cheap iron metal has been demonstrated. The present low cost method is superior to the use of catalysts such as Pd/C and raney nickel under high pressure. The reported method is superior with respect to yield, reaction duration and purity of the desired compounds. In addition to this, 4'-(β-naphthol azo benzo)-18-crown-6, 4a shows a selective molecular recognition behavior toward barium(II) and calcium(II) ions over the some alkaline earth metals. This introduces the new and selective chromogenic probe for sensing barium(II) and calcium(II) ion in chemical system. The prepared 4'-β-naphthol azo benzo)-18-crown-6, 4a can be used as a new and selective chromogenic probe for the sensing the barium(II) and calcium(II) ion in chemical system.

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