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Synthesis of new sulfone containing aza oxa crowns

Esmael Rostami

Department of Chemistry, Payame Noor University, PO BOX 19395-3697, Tehran, (IRAN)

E-mail: Esmrostami@yahoo.com

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ABSTRACT

New sulfone containing aza crowns bearing naphthalene were prepared. At first sulfone diester was synthesized from corresponding sulfide. Aza crowns were synthesized efficiently from the reaction of sulfone diester and diamines under microwave conditions.

KEYWORDS

Aza oxa thia crowns;
Macrocycle;
Synthesis;
Naphthalene;
Microwave;
Sulfone.

INTRODUCTION

Since the pioneering work of Pedersen in 1967[1], crown ethers and aza crowns have gained significant interest in the context of phase transfer catalysts, biological ion transfer, molecular switches and a series of applications such as sensors or biological model systems[2]. Crown ethers are compounds that, are cyclic oligomers of ethylene oxide. Pedersen examined dibenzo-18-crown-6 and similar crown ethers and showed that the receptor and guest ion can interact and form stable complexes[1].

A large number of research groups developed the new crown ethers and aza crowns[3]. Introduction of other elements such as N and S improve the complexation properties of crown ethers[4]. In recent years, crown ether and aza crown chemistry led to a large number of receptors such as cyclic peptides[5], calixarenes[6], cryptands[7], lariat ethers[8] and polymer containing crowns[9]. Many different methods were described for the synthesis of crown ethers. Five methods with different starting materials were reported by Pedersen[1]. Instead of diols for the synthesis of crown ethers, dicarboxylic acids[10], amines[2], thiols can be used[11] and metal transition salts can catalyze the reactions[12]. Also, related families like the aza-crowns, aza oxa crowns, aza oxa thia crowns, cryptands, calixarenes and other macrocyclic groups were developed via different routes such as the reaction of diamines and dicarboxylic acids, diamines and diacid chlorides, phenols and formaldehyde, and related synthetic methods[13-15].

The crown ethers and aza crowns are known for their ability to strongly enhance cation solubility in organic solvents. The oxygen, nitrogen and sulfor atoms are ideally situated to coordinate with a cation inside the ring, whereas the outside of the ring is hydrophobic. The result of this hydrophilic heart-hydrophobic shell is that the complexed cation is soluble in nonpolar solvents. The size of the inner ring of the macrocycle determines the size of the cation it can solvate. Therefore, 18-crown-6 has high affinity[2] for the potassium cation, 15-crown-5 for the sodium cation and 12-crown-4 for the lithium cation. Besides the relative sizes of the ion and the hole in the macrocycle ring, some other fac-

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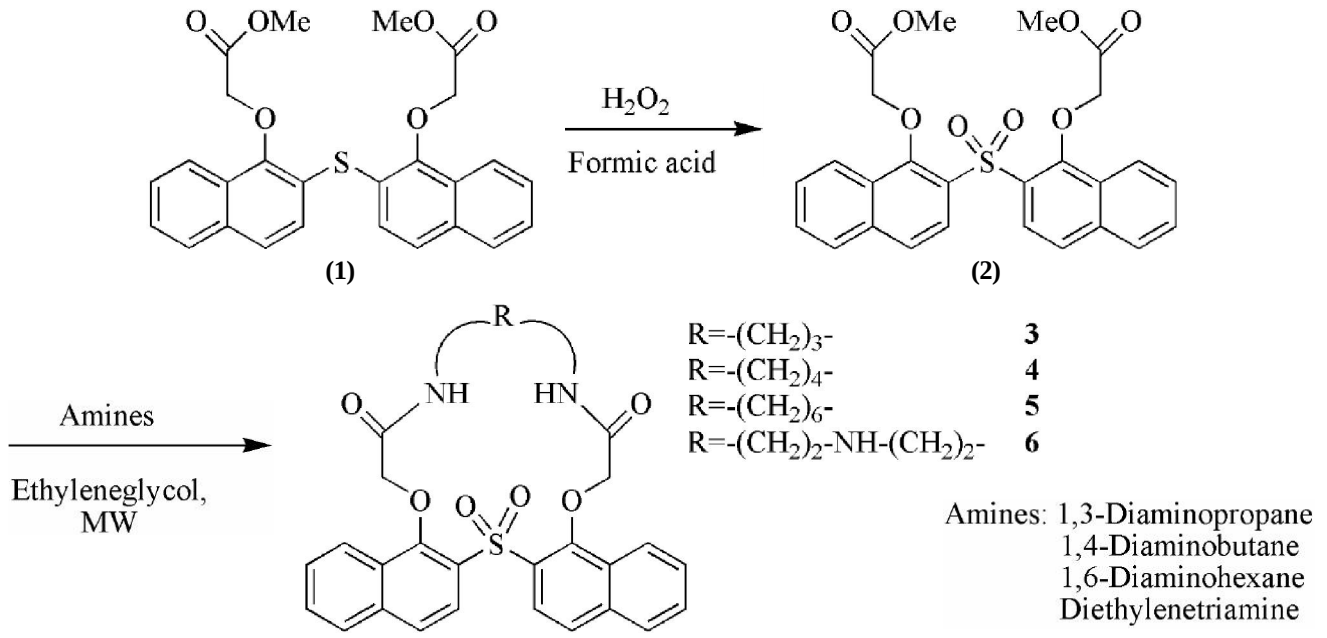
tors enhance complexation such as the number of donor atoms (O,N,S) in the macrocycle ring, the coplanarity of the donor atoms, the symmetrical placement of the donor atoms, the basicity of atoms, steric hindrance in the ring, the tendency of the ion to associate with the solvent and the electrical charge of the ion[2].

Aza crowns and related macrocycles can be integrated in a larger structures such as polymers or be the central core of a dendrimer unit. These structures lead to applications in nanotubes and nanostructures[16] or optical devices[17]. Attached of macrocycles to silica and other solid supports, affords modified supports with new efficiency and applications that can be used in separations such as in chromatography[18].

In continuation of our researches on the synthesis of aza crowns[19], in this research work new dinaphthosulfone aza crowns were prepared under microwave irradiation, from the reaction of diesters and diamines in ethyleneglycol in good yields.

EXPERIMENTAL

The reactions were carried out in an efficient hood cupboard. All the materials were purchased from Merck, Fluka, Across Organics and Aldrich chemical companies. Acetonitrile was distilled and stored over molecular sieves. DMF was distilled over molecular sieves under reduced pressure and stored over them. Merck silica gel 40 was used for column chromatography. Merck silica gel 60 F254 TLC plates were used for thin layer chromatography (TLC). The melting points (uncorrected) were measured with an Electrothermal engineering LTD 9100 apparatus. Elemental analysis was performed by a CHN-O- Rapid Heraeus elemental analyzer. IR spectra were measured on a FT-IR BRUKER spectrometer. The ^1H NMR and ^{13}C NMR spectra were obtained using BRUKER AVANCE DRX 500 MHz apparatus and mass spectra were obtained with Shimadzu GC-MS-QP 1100



Scheme 1 : Synthesis of aza crowns (3-6).

EX model. A Microsynth apparatus was used for microwave irradiation.

Synthesis of 2, 2'-Sulfoxobis-(1-naphthoxy (2-methyl acetate)) (2)

To a mixture of 1[19a] (2mmol, 0.92g) and formic acid (50ml) at 0ºC was added hydrogen peroxide (4mmol, 0.44ml), and stirred at room temperature for 12h. After completion of the reaction (monitored by TLC), water was added and the resulting mixture was filtered, washed with water, dried and recrystallized in Ethanol/THF to afford a white powder (2) in 94% yields, and melting point of 204-205 ºC; IR (KBr): 3152, 3073, 2934, 2941, 2863, 1748, 1617, 1586, 1539, 1515, 1449, 1418, 1336, 1326, 1285, 1250, 1214, 1142, 1121, 1094, 1053, 990, 974, 813, 591 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 3.32 (s, 3H, CH_3), 3.46 (s, 3H, CH_3), 4.29 (s, 4H, CH_2), 7.35 (d, J = 10 Hz,

2H, Ar), 7.50 (dd, J = 7.5, 10 Hz, 2H, Ar), 7.66 (dd, J = 7.5, 10 Hz, 2H), 7.96 (d, J = 10 Hz, 2H, Ar), 8.15 (d, J = 9 Hz, 2H, Ar), 9.39 (d, J = 9 Hz, 2H, Ar) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.66, 157.00, 136.39, 134.02, 131.18, 129.85, 129.60, 129.17, 127.98, 126.16, 125.32, 124.03, 116.16, 52.53 ppm; MS EI (electron impact) m/z (relative intensity, %): 494 $[M]^+$ (7), 462 (36), 316 (11), 283 (25), 216 (54), 187 (43), 144 (37), 127 (62), 115 (100), 64 (17), 45 (76); Anal. Calcd. for $C_{26}H_{22}O_8S$ (494.1): C, 63.15; H, 4.48. Found: C, 63.18; H, 4.47.

General procedure for the synthesis of dinaphthosulfone aza crowns (3-6)

To ethyleneglycol (10mL), were added diester (2, 2mmol, 0.98g) and appropriate diamine (2mmol) at room temperature. The resulting mixture was stirred at room temperature for 10 Min., and then irradiated in 500w using microwave conditions for 9 Min. (3×3 Min.) and rest time of 10 Min. (2×5Min.). After completion of the reaction (TLC), the reaction mixture was allowed to cool to room temperature, water was added and the resulting mixture was extracted with chloroform (3×50mL). The combined chloroform layers, were dried and evaporated to afford a precipitate that purified by column chromatography on silica gel using appropriate solvent mixtures as eluent.

Synthesis of 7, 11 -diaza-1-sulfoxo- 4, 14-dioxa- 6, 12-dioxo - 2, 3; 15, 16 -dinaphtho-cyclohexadecane (3)

This aza crown was prepared based on the general procedure by the reaction of 2 (2mmol, 0.98g), and 1,3-diaminopropane (2mmol, 0.17mL) under microwave irradiation, and purified by column chromatography on silica gel using dichloromethane/methanol (3:1) as eluent to afford 3 as white solid in 68% yield, mp 211-212°C; IR (KBr): 3411, 3332, 3068, 2919, 1691, 1632, 1597, 1547, 1481, 1391, 1267, 1228, 1143, 1068, 1028, 754 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.68–1.73 (m, 2H), 3.03–3.09 (m, 4H), 4.71 (s, 4H), 7.39-7.41 (m, 4H), 7.46 (dd, J = 9, 10 Hz, 2H), 7.86-7.89 (m, 2H), 7.93 (d, J = 8 Hz, 2H), 8.15 (d, J = 9 Hz, 2H), 8.84 (d, J = 9 Hz, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 165.73, 155.56, 131.93, 128.68, 127.96, 127.16, 126.83, 125.54, 124.36, 123.22, 115.31, 68.32, 63.71, 63.56 ppm; MS EI (electron impact) m/z (relative intensity, %): 504 [M]+ (16), 434 (23), 330 (34), 300 (26), 283 (100), 257 (67), 211 (19), 126 (11), 99 (15); Anal. Calcd. for $C_{27}H_{24}N_2O_6S$ (504.14): C, 64.27; H, 4.79; N, 5.55 Found: C, 64.25; H, 4.78; N, 5.58.

Synthesis of 7, 12-diaza-1-sulfoxo- 4, 15-dioxa-6, 13-dioxo - 2, 3; 13, 14-dinaphtho-cycloheptadecane (4)

This aza crown was synthesized based on the general procedure by the reaction of 2 (2mmol, 0.98g), and 1,4-diaminobutane (2mmol, 0.20mL) under microwave irradiation, and purified by column chromatography on silica gel using chloroform/methanol (4:1) as eluent to afford 4 as a white solid in 65% yield, mp 198-199°C; IR (KBr): 3358, 3074, 2934, 2896, 1699, 1673, 1629, 1591, 1553, 1519, 1474, 1348, 1285, 1169, 1127, 1083, 1026, 975, 811cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.25-2.36 (b, 4H), 4.04–4.05 (b, 4H), 4.35 (d, J = 17 Hz, 2H), 4.50 (d, J = 17 Hz, 2H), 7.22 (d, J = 10Hz, 2H), 7.47 (m, 2H), 7.57 (dd, J = 7.8, 10 Hz, 2H), 7.63 (dd, J = 8,10 Hz, 2H), 7.92 (d, J = 7.5 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H), 9.23 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.78, 158.12, 136.45, 134.29, 132.05, 129.11, 128.53, 128.16, 127.84, 125.79, 125.34, 124.63, 117.33, 68.49, 64.14, 63.65, 63.17 ppm; MS EI (electron impact) m/z (relative intensity, %): 518 [M]+ (14), 484 (25), 483 (12), 318 (18), 299 (10), 254 (13), 145 (15), 58 (34), 55 (61), 43 (100); Anal. Calcd. for $C_{28}H_{26}N_2O_6S$ (518.15): C, 64.85; H, 5.05; N, 5.40 Found: C, 64.87; H, 5.04; N, 5.43.

Synthesis of 7,14-diaza-1-sulfoxo-4,17-dioxa-6,15-dioxo-2,3;18,19-dinaphtho-cyclononadecane (5)

This aza crown was prepared based on the general procedure by the reaction of 2 (2mmol, 0.98g), and 1,6-diaminohexane (2mmol, 0.24g) under microwave irradiation, and purified by column chromatography on silica gel using chloroform/methanol (4:1) as eluent to afford 5 as a white solid in 58% yield, mp 187-188°C; IR (KBr): 3475 (NH amide), 3283, 2936, 1689 (carbonyl), 1559, 1417, 1285, 1097, 1043, 884 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.45-3.47 (b, 4H, CH_2), 4.27-4.29 (b, 8H, CH_2), 4.46 (d, J = 16.5 Hz, 2H, CH_2), 4.50 (d, J = 17 Hz, 2H, CH_2), 7.35 (d, J = 8.5 Hz, 2H, Ar), 7.44-7.45 (m, 1H), 7.49-7.52 (m, 2H), 7.53-7.55 (m, 1H), 7.65-7.67 (m, 2H), 7.96 (d, J = 8Hz, 2H), 8.15 (d, J = 8.5 Hz, 2H), 9.39 (d, J =

8.5 Hz, 2H, Ar) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ = 168.54 (carbonyl), 157.18, 138.73, 135.11, 132.39, 129.81, 128.95, 128.24, 128.19, 127.76, 128.01, 125.35, 116.87, 68.33, 68.25, 64.11, 63.54, 46.67, 44.72, 41.17, 39.65 ppm; MS EI (electron impact) m/z (relative intensity, %): 546 $[M]^+$ (8), 434 (54), 316 (14), 300 (73), 271 (12), 187 (74), 144 (41), 115 (100), 88 (22), 69 (27), 44 (33); Anal. calcd. for $C_{30}H_{30}N_2O_6S$ (546.18): C, 65.92; H, 5.53; N, 5.12. Found: C, 65.91; H, 5.54; N, 5.14.

Synthesis of 7, 10, 13-triaza-1-sulfoxo-16, 4-dioxa-6, 14-dioxo-2, 3; 17, 18-dinaphtho-cyclooctadecane (6)

This aza crown was synthesized based on the general procedure by the reaction of 2 (2mmol, 0.98g), and diethylenetriamine (2mmol, 0.22mL) under microwave irradiation, and purified by column chromatography on silica gel using chloroform/methanol (4:1) as eluent to afford 6 as a white solid in 75% yield, mp 271-272°C; IR(KBr): 3361, 3076, 2943, 1689, 1514, 1468, 1433, 1345, 1286, 1138, 1089, 818 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.53-2.55 (b, 4H), 3.14-3.16 (b, 4H), 4.74 (s, 4H), 7.42-7.44 (m, 4H), 7.49 (dd, J = 9,10 Hz, 2H), 7.91-7.93 (b, 2H), 7.96 (d, J = 8 Hz, 2H), 8.23 (d, J = 8.5 Hz, 2H), 8.86 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.84, 156.40, 137.65, 130.70, 130.29, 129.76, 129.50, 125.41, 123.30, 123.08, 114.91, 68.48, 63.67, 46.73, 38.41 ppm; MS EI (electron impact) m/z (relative intensity, %): 533 $[M]^+$,(molecular ion) (8), 300 (43), 287 (11), 216 (44), 187 (22), 144 (100), 128 (12), 115 (35), 44 (25); Anal. Calcd. for $C_{28}H_{27}N_3O_6S$ (533.16): C, 63.03; H, 5.10; N, 7.87. Found: C, 62.598; H, 5.09; N, 7.90.

RESULTS AND DISCUSSION

2, 2'-thiobis-(1-naphthoxy (2-methyl acetate)) (1)

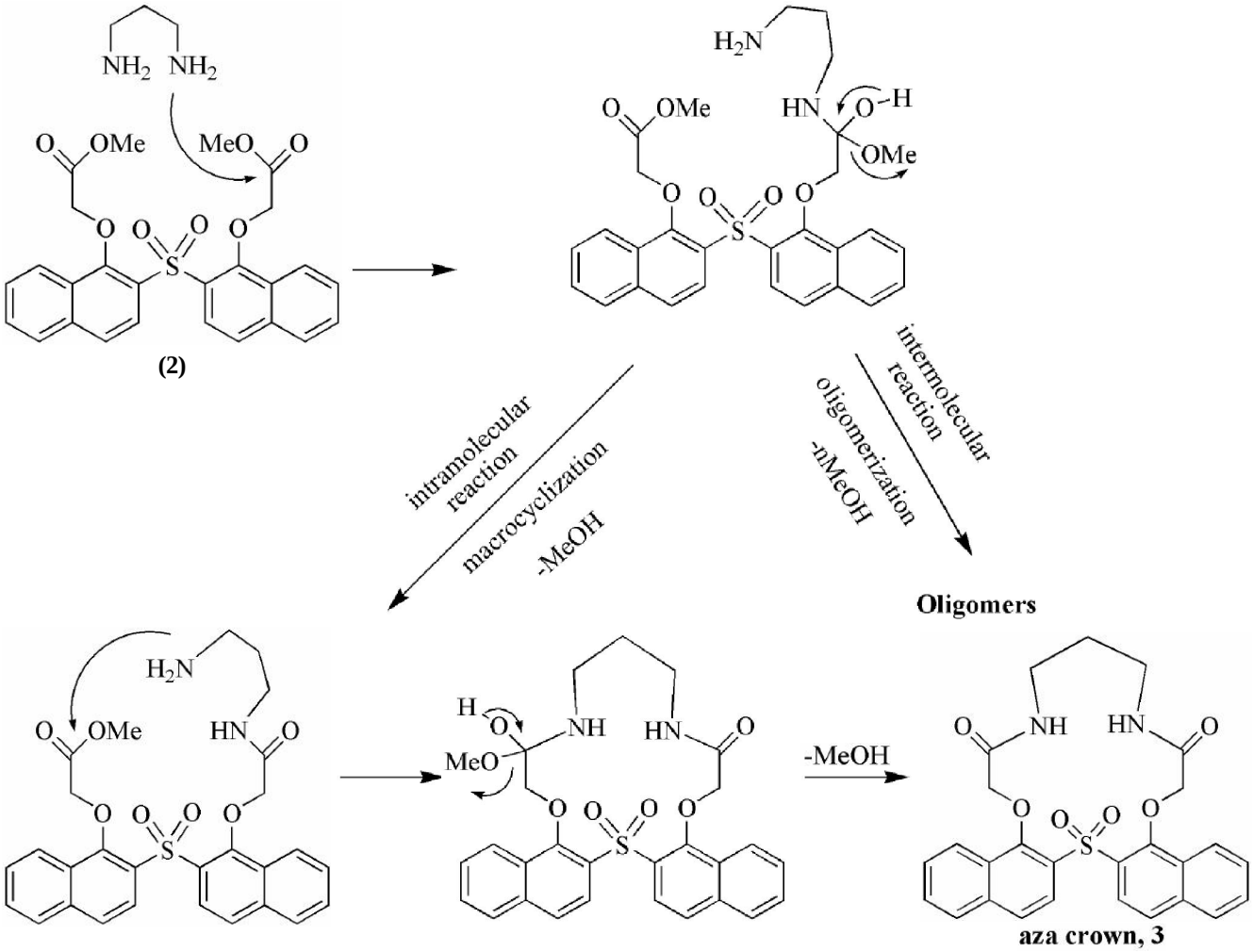


Figure 1 : Proposed mechanism for the synthesis of 3.

was prepared based on the reported procedure[19a]. 2, 2'-Sulfoxobis-(1-naphthoxy (2-methyl acetate)) (2) was prepared from the reaction of 1 and hydrogen peroxide in formic acid. Aza crowns (3-6) were synthesized from the reaction of diester (2) and various aliphatic diamines under microwave irradiation (MW) in good yields (Scheme 1).

Reaction of diesters and diamines performed via two reaction rutes: macrocyclization and oligomerization (or polymerization). Macrocyclization is the synthesis of cyclic products and the yield of this route is governed by a series of factores such as the size of prepared macrocycle, size of diamine, the structure of diester, reaction conditions such as concentration of medium, steochiometry of reaction. By the change in each of these factors macrocyclization or oligomerization overcomes and the yield of macrocycle will change. The yields of macrocycles under microwave irradiation are good to reliable, and as a result the macrocyclization route is preferred to oligomerization under these conditions.

Mechanism of aza crown (3) formation is appeared in figure 1. In this mechanism from the reaction of diester and diamine led to a linear intermediate that aza crowns were prepared via macrocyclization route and oligomers via oligomerization route.

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