Research Article

BINOL Macrocycle Derivatives: Synthesis of New Dinaphthyl Sulfide Aza Oxa Thia Crowns (Lariats)

Abbas Shockravi,1,2 Shahram Mehdipour-Ataei,3 and Esmael Rostami4

1 Faculty of Chemistry, Tarbiat Moallem University, Mofatteh Avenue, No. 49, Tehran 15614, Iran
2 Faculty of Chemistry, Tarbiat Moallem University, 31979-37551, Karaj, Iran
3 Polyurethanes & Advanced Polymeric Materials Department, Faculty of Polymer Science, Iran Polymer & Petrochemical Institute (IPPI), P.O. Box 14965/115, Tehran, Iran
4 Department of Chemistry, Payame Noor University, P.O. Box 19395-3697, Tehran 19569, Iran

Correspondence should be addressed to Esmael Rostami; esmaelrostami@gmail.com

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In this research work, dinaphthyl sulfide diester was prepared from the reaction of 1,1′-thiobis (2-hydroxy naphthalene) and methylchloroacetate. Its aza-macrocyclic derivative was synthesized from the reaction of dinaphthyl sulfide diester and diethylenetriamine. Lariats were prepared from the reaction of chloroamides (four derivatives) and initial macrocycle. Chloroamides were synthesized from the reaction of amines (aniline, benzylamine, 8-amino quinoline and 4-amino azobenzene) and chloroacetyl chloride. All the materials were identified by IR, 1H NMR, 13C NMR, and mass spectroscopies, and elemental analysis.

1. Introduction

Since the initial publications on the synthesis of crown ethers and their metal salt complexation properties [1, 2], the influence of structural variation within such ligands has received increasing attention [3–12]. One such structural variation is the replacement of one ether oxygen with nitrogen to give an azacrown ether [13, 14] or sulfur group to obtain thiacrown ether [14, 15]. Another is the attachment of a functional side arm to the ligand framework to provide the potential for three-dimensional complexation of metal ions. Such armed crown ethers have been designated as lariat ethers [16–18]. If the side arm attachment site is a carbon atom of the macrocycle, the ligand is called a C-pivot lariat ether. If it is a nitrogen atom of azacrown ether, the ligand is identified as a N-pivot lariat ether.

Efficient syntheses of N-pivot lariat ethers in which phenolic and hydroxyquinoline units are attached to an aza crown ether nitrogen by a methylene group have been developed using the Mannich reaction [19]. A lot of lariat aza-macrocycles were synthesized in which their side chain containing several functional groups such as ether [20], amide [21, 22], acid [23], nitrogen [24], and other functional groups that have an active role in binding properties towards various kinds of guests.

BINOL is an important building block in chemistry. A large number of BINOL derivatives have been explored, and important BINOL derivatives are BINOL crown ethers and macrocycles. The study of optically active BINOL compounds and the new derivatives of these compounds is an active route in organic synthesis in recent years [25–32]. According to the Figure 1, BINOL and dinaphthyl sulfides are derivatives. In the dinaphthyl sulfides structure, sulfur atom is a strong donor atom for complexation properties and as a result dinaphthyl sulfide has stronger donor atoms in comparison with BINOL. Several works were performed for the application of dinaphthyl sulfide derivatives (podands and aza crowns): the study of complex formation with silver atoms [33], complexation with Pb2+, Ni2+, and Hg2+ [34], Hg2+ [35], Pb2+ [36], Ag+ [37], Cu2+ [38]. Dinaphthyl sulfide aza crowns diffuse across the cell membranes and interfere with
different living systems [39]. All of these research works show that the dinaphthyl sulfide receptors have a large number of applications in chemistry and related areas.

In this research work, new dinaphthyl sulfide lariats were prepared. These compounds are the aza oxo thia crowns bearing napthol building blocks. The study of these compounds and their derivatives is underway.

2. Experimental

The reactions were carried out in an efficient hood. All the materials were purchased from Merck, Fluka, and Aldrich chemical companies. Methanol and dichloromethane were distilled and stored under Lind 4Å molecular sieves. Compounds 1 were synthesized based on the reported procedure [33–38]. Two chloroamides (6 and 7) were reported previously [40–42]. The melting points (uncorrected) were measured with an Electrothermal Engineering Ltd. 9100 apparatus. Elemental analysis was performed on a CHN–O– Rapid Heraeus elemental analyzer. IR spectra were measured on a Perkin-Elmer model 543, the 1H NMR and 13C NMR spectra were obtained using Bruker Avance DPX 300 MHz and Bruker Avance DRX 500 MHz apparatus, and mass spectra were obtained using Shimadzu GC-MS-QP 1100 EX model.

2.1. General Procedure (1), the Synthesis of α-Chloroamide Derivatives (4–7). To a vigorously stirred solution of amine (2 mmol) and triethylamine (2 mmol) in an appropriate dried solvent (50 mL, CH2Cl2 or CH3CN) a solution of chloroacetyl chloride (2 mmol) was added in the same solvent (50 mL) at 0°C. The reaction mixture was stirred at room temperature for 6h. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with distilled water (50 mL) and then was extracted with CH2Cl2 (2 × 50 mL). The combined organic layers were washed with 10% aqueous HCl solution (50 mL) and water (50 mL), dried (Na2SO4), and evaporated to afford crude products which were purified by recrystallization from ethanol.

2.1.1. Synthesis of 3-Aza-2-oxo-3-phenyl-propyl chloride (4). This chloroamide (4) was prepared from the reaction of aniline and chloroacetyl chloride based on the general procedure (1) and afforded as a white powder in 94% yield, mp 94–95°C; IR (KBr): 3266, 3069, 2978, 1657, 1601, 1547, 1483, 1444, 1418, 1365, 1343, 1231, 1199, 1104, 927, 785 cm−1; 1H NMR (300 MHz, CDCl3) δ: 4.18 (s, 2H), 7.18 (tt, J = 9, 1.2 Hz, 1H), 7.37 (ddd, J = 9, 3, 1.8 Hz, 2H), 7.56 (dt, J = 6, 3 Hz, 2H), 8.24 (b, 1H) ppm; 13C NMR (75 MHz, CDCl3): δ 49.36, 126.25, 127.82, 128.75, 142.34, 164.79 ppm; Anal. Calcd. for C13H15ClNO: C, 58.84; H, 5.50; N, 7.65. Found: C, 58.84; H, 5.50; N, 7.65.

2.2. General Procedure (2), the Synthesis of Lariats (8–11). To macrocycle (3) (1 mmol, 0.50 g) in acetonitrile (50 mL) alkylating agents were added (one of the chloroamides (4–7) for each reaction) (1 mmol), sodium carbonate (1 mmol, 0.14 g), sodium iodide (catalytic), and dimethylformamide (DMF, 5 mL). The resulting mixture was stirred at room temperature for 24h. After completion of the reaction (monitored by TLC), water (50 mL) was added, the mixture was extracted with chloroform (3 × 50 mL), and washed with HCl (10%, 2 × 50 mL), respectively; the combined chloroform layers were dried (Na2SO4) and evaporated to afford crude product which was purified by column chromatography on silica gel.

2.2.1. Synthesis of 7,10,13-Triaza-1-thia-16,4-dioxo-10-(3-aza-2-oxo-3-(8-quinolyl) propyl)-6,14-dioxo-2,3,17,18-dinaphthyl-cyclooctadecane (8). This azacrown (8) was synthesized from the reaction of quinoline chloroamide (6) and macrocycle (3) based on the general procedure (2) and purified by column chromatography on silica gel using CH2Cl2/Methanol (3:1) as eluent, the yield was 76% and mp 230–231°C; IR (KBr): 3407, 3348, 3069, 2954, 2843, 1686, 1670, 1596, 1533, 1534, 1510, 1419, 1430, 1329, 1280, 1092, 1031, 813 cm−1; 1H NMR (300 MHz, CDCl3) δ: 7.21 (s, 4H), 3.33 (s, 4H), 3.46 (s, 2H), 4.47 (s, 4H), 7.23–7.30 (m, 3H), 7.35–7.45 (m, 5H), 7.53 (d, J = 6 Hz, 1H), 7.77 (d, 2H), 7.90 (d, J = 9 Hz, 4H), 8.23 (d, 1H, J = 6 Hz), 8.25 (d, J = 3 Hz, 1H), 8.37 (d, J = 9 Hz, 2H), 8.81 (d, J = 3 Hz, 1H), 10.21 (s, 1H) ppm; 13C NMR (75 MHz, DMSO-d6): δ: 169.85, 167.15, 155.94, 148.88, 137.91, 136.45, 134.12, 133.89, 132.80, 129.18, 129.47, 128.70, 127.67, 127.34, 126.70, 124.15, 124.09, 121.88, 121.74, 117.16, 116.38, 114.84, 68.00, 58.47, 53.61, 36.55 ppm; MS (EI) m/z: 685 [M]+ (4%), 648 (6%), 514 (13%), 300 (5%), 216 (25%), 187 (28%), 144 (100%), 115 (63%), 91 (8%), 63 (8%); Anal. Calcd. for C35H34N6O8S: C, 68.30; H, 5.14; N, 20.12. Found C, 68.27; H, 5.15; N, 10.23.
2.2.2. Synthesis of 7,10,13-Triaza-1-thia-16,4-dioxa-10-(3-aza-2-oxo-4-phenyl butyl) propyl)-6,14-dioxo-2,3,17,18-dinaphthyl-cyclooctadecane (9). This aza crown (9) was synthesized from the reaction of azobenzene chloroamide (7) and macrocycle (3) based on the general procedure (2) and purified by column chromatography on silica gel using CH₂Cl₂/Methanol (4:1) as eluent, the yield was 85% and mp 251-252°C; IR (KBr): 3406, 3074, 2951, 1686, 1671, 1601, 1546, 1511, 1468, 1447, 1435, 1417, 1256, 1230, 1159, 1079, 1032, 784, 693, 564 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ: 2.64 (s, 2H), 3.31–3.33 (m, 6H), 4.41 (s, 4H), 4.59 (s, 2H), 6.81–7.59 (m, 12H), 7.90 (s, 9H), 8.36 (d, 1H), 8.44 (d, 2H) ppm; ¹³C NMR (75 MHz, DMSO-d₆) δ: 167.58, 156.10, 151.99, 134.18, 133.99, 131.03, 130.13, 129.52, 129.40, 128.65, 127.36, 124.07, 123.66, 123.52, 122.32, 119.87, 119.76, 119.10, 118.84, 116.74, 115.00, 114.68, 68.11, 67.71, 45.78, 36.68 ppm; MS (EI) m/z: 738 [M⁺]⁺ (7%), 475 (9%), 474 (12%), 434 (18%), 385 (22%), 377 (15%), 370 (13%), 369 (15%), 300 (13%), 289 (19%), 264 (15%), 226 (5%), 224 (6%), 197 (74%), 184 (22%), 144 (10%), 120 (41%), 92 (77%), 91 (100%), 90 (52%), 77 (85%), 66 (33%), 65 (69%), 52 (53%), 39 (42%); Anal. Calcd. for C₅₂H₄₅N₂₀₂S: C, 68.27; H, 5.18; N, 11.37. Found C, 68.26; H, 5.19; N, 11.40.

2.2.3. Synthesis of 7,10,13-Triaza-1-thia-16,4-dioxa-10-(3-aza-2-oxo-4-phenyl butyl) propyl)-6,14-dioxo-2,3,17,18-dinaphthyl-cyclooctadecane (10). This aza crown (10) was synthesized from the reaction of macrocycle (3) and benzyl amine chloroamide (5) based on the general procedure (2) and purified by column chromatography on silica gel using CH₂Cl₂/Methanol (4:1) as eluent, the yield was 83% and mp 228-229°C; IR (KBr): 3392, 3070, 2946, 2872, 1683, 1628, 1595, 1538, 1509, 1466, 1433, 1357, 1328, 1274, 1229, 1155, 1084, 1031, 815, 760 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ: 2.58 (s, 4H), 3.03 (s, 2H), 3.18 (s, 4H), 3.95 (s, 2H), 4.41 (s, 4H), 7.02 (s, 1H), 7.20–7.44 (m, 11H), 7.58 (s, 1H), 7.85 (dd, J = 9.2, 15.2 Hz, 4H), 8.05 (s, 1H), 8.38 (d, J = 8.4 Hz, 2H) ppm; ¹³C NMR (75 MHz, DMSO-d₆) δ: 170.05, 167.41, 155.97, 139.17, 134.12, 130.21, 129.43, 128.65, 128.31, 128.15, 127.34, 127.18, 127.12, 126.88, 126.67, 124.15, 124.06, 117.16, 114.67, 67.93, 56.14, 52.93, 42.44, 41.63, 36.20, 30.94 ppm; MS (EI) m/z: 649 [M⁺]⁺ (5%), 648 [M⁺]⁺ (7%), 516 (8%), 515 (17%), 514 (100%), 501 (5%), 318 (1%), 300 (26%), 216 (30%), 187 (49%), 144 (77%), 115 (75%), 91 (100%), 85 (48%), 77 (12%), 65 (18%), 42 (49%); Anal. Calcd. for C₅₂H₄₅N₂₀₂S: C, 68.50; H, 5.59; N, 8.64. Found C, 68.53; H, 5.58; N, 8.66.

2.2.4. Synthesis of 7,10,13-Triaza-1-thia-16,4-dioxa-10-(3-aza-2-oxo-3-phenyl benzene) propyl)-6,14-dioxo-2,3,17,18-dinaphthyl-cyclooctadecane (11). This aza crown (11) was synthesized from the reaction of macrocycle (3) and aniline chloroamide (4) based on the general procedure (2) and purified by column chromatography on silica gel using CHCl₃/Methanol (4:1) as eluent, the yield was 89% and mp 222-223°C; IR (KBr): 3385, 3054, 2936, 1688, 1679, 1623, 1601, 1558, 1540, 1503, 1446, 1323, 1263, 1225, 1079, 765 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆) δ: 3.49 (b, 4H), 3.62 (s, 4H), 4.27 (b,
Scheme 3: Synthesis of lariats (8–11).

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Figure 2: Proposed mechanism for the formation of macrocycle (3).
2H), 4.38–4.54 (two doublets, 4H, \( J = 12, 18 \) Hz), 7.13 (b, 1H), 7.32–7.48 (m, 4H), 7.61 (b, 2H), 7.88–7.92 (dd, 1H, \( J = 9 \) Hz), 8.40 (d, 1H, \( J = 18 \) Hz), 9.10 (b, 1H), 10.90 (b, 1H) ppm; \( ^{13}C \) NMR (75 MHz, DMSO-\( d_6 \)): 169.53, 155.73, 134.06, 129.98, 129.37, 128.94, 128.62, 127.30, 124.15, 124.07, 119.48, 114.52, 67.25, 55.66, 53.95, 34.17 ppm; MS (EI) m/z: 634 [M]+, 216 (26%), 318 (11%), 93 (24%), 77 (12%), 63 (28%), 39 (27%); Anal. Calcd. for C_{34}H_{46}N_{12}O_{12}S: C, 68.12; H, 5.40; N, 8.83. Found C, 68.10; H, 5.41; N, 8.84.

3. Results and Discussion

The key step in this project is the synthesis of aza-macrocyle (3). Dinaphthol (1) was synthesized from the reaction of 2-naphthol and sulfur dichloride based on the reported procedure [40–42]. The corresponding diester (2) was synthesized according to the modified reported procedure from the reaction of 1 and methylichloroacetate in the presence of potassium carbonate and catalytic amounts of KI in CH\(_3\)CN and DMF (10:1) solvent mixture at room temperature [43, 44]. Macrocyle (3) was synthesized from the reaction of diester (2) and diethylenetriamine in the presence of catalytic amounts of p-toluene sulfonic acid (p-TsOH) in methanol (Scheme 1) [43]. The proposed mechanism for the formation of macrocycle (3) is appeared in Figure 2.

Chloroamide derivatives (4–7) were synthesized from the reaction of corresponding amine and chloroacetyl chloride in the presence of triethylamine as base and in dichloromethane as solvent (Scheme 2) [40–42, 45], the lariat azacrowns (8–11) were synthesized from the reaction of chloroamines (4–7) and macrocycle (3). This reaction was carried out via a modified procedure in the presence of sodium carbonate and catalytic amounts of sodium iodide in CH\(_3\)CN/DMF (10:1) at room temperature (Scheme 3) [46–48].

According to the previous works [33–38] on the applications of dinaphthyl sulfide receptors in host-guest chemistry, these new receptors are important candidates for a large number of studies such as complexation with metal ions, biological systems, and the applications in the preparation of nanostructures [44].

4. Conclusions

To summarize, we prepared a dinaphthyl sulfide aza crown, and then new dinaphthyl sulfide aza lariats (8–11) were prepared from the reaction of aza crown and some prepared chloroamides. This lariat is important receptors with naphthalene, quinolone, and azo groups. Based on the reported applications, the new receptors with pendant arms are strong complexation abilities and are potential candidates for host-guest chemistry and related areas.


