Efficient synthesis of dihydrazide crown ethers by fast addition method

Hossein Eshghi[a]*, Mehdi Bakavoli[a] and Mosayyeb Hosseini[b]

[a]*Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 91775-1436, Iran*

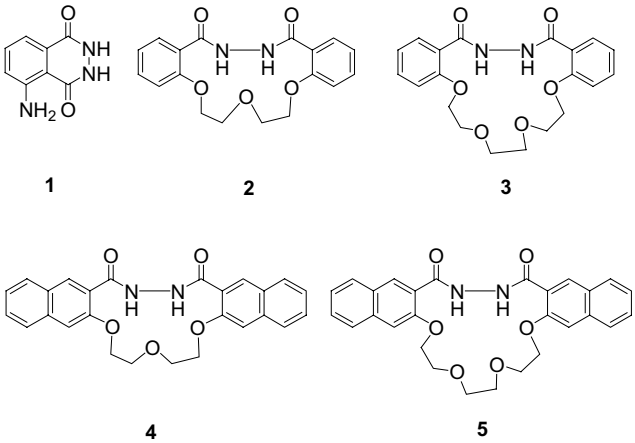
[b]*Department of Chemistry, Sistan and Baluchestan University Zahedan 98135-674, Iran*

The novel macrocyclic dihydrazides which structurally related to luminal were synthesised. These compounds were obtained in the macrocyclisation step by fast addition method and the results were compared with solvent-free conditions.

Keywords: solvent free conditions, macrocyclisation, fluorescence, dilactam, fast addition

Recently, much attention has been paid to the fluorometric sensing of a specific molecule based on the host–guest interaction.[1] Light emitting fragments such as naphthalene,[2] anthracene,[3] pyrene,[4] isoquinoline-*N*-oxide,[5] flavone,[6] and binaphthyl[7] groups have often been used as an excellent fluorescence probe on account of their high sensitivity for detector. Although, a wide variety of compounds are known to be fluorescent, but probably the best known example at this category is the oxidation of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione, **1**) to give an intense blue light, first reported by Albrecht in 1928.[8] A large number of related hydrazides have since been tested; both cyclic and acyclic hydrazides are fluorescent.[9]

Here we report the synthesis of novel macrocyclic dihydrazides (**2**–**5**) which structurally related to luminol and would be apply as fluorescence sensors. These compounds were obtained in the macrocyclisation step by fast addition method in moderate yields (Scheme 1).



Scheme 1

Results and discussion

One of the most common and conventional methods of constructing macrocyclic lactams is to utilise the reaction of dicarboxylic acid chlorides with diamines. This route is indeed effective, especially with simple acyl chlorides that are readily purified and in cases of less reactive diamines. Adverse factors, however, arise in the generally low yields and difficulty in purifying larger acyl chlorides. Furthermore, high-dilution techniques[10,11] are necessary in most cases to perform such reactions, in order to obtain reasonable yields because of a tendency to form linear polyamides. Moreover, besides the desired one-to-one adduct, two-to-two cyclisation products were sometimes obtained,[12] which increased the problems of purification. Recently, we have reported that, high dilution technique is not required for the reaction of diacid chloride with diamines to form macrocyclic dilactams.[13-14]

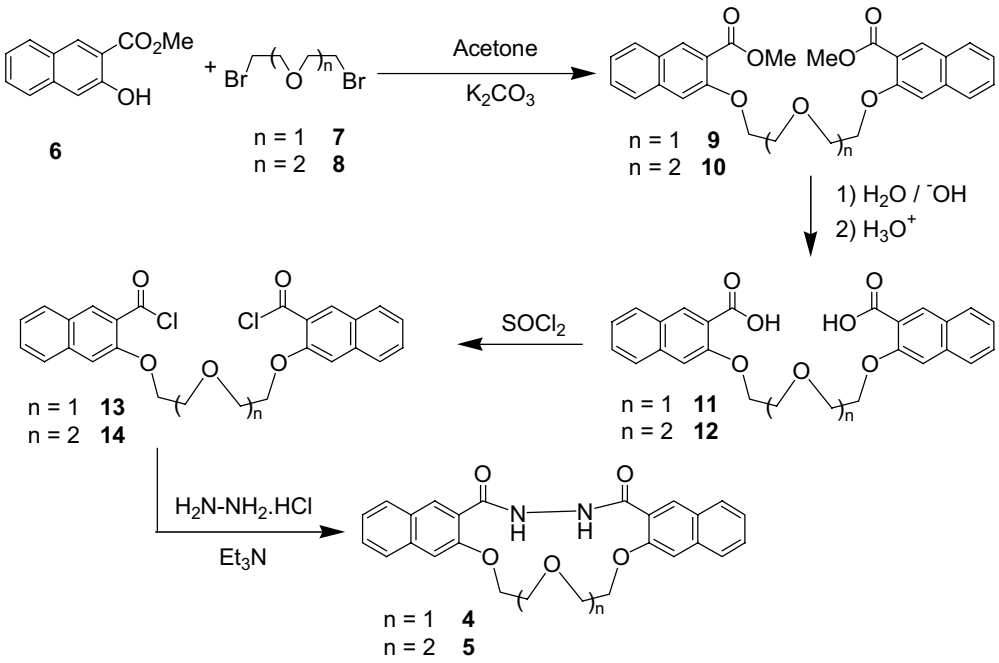
The reaction of 3-hydroxy-2-methylnaphthoate **6** with dibromides **7** and **8** in acetone using potassium carbonate as the base resulted in formation of diesters **9** and **10** in 80 and 96% yields respectively. Dicarboxylic acids **11** and **12** were obtained quantitatively by saponification of diesters followed by acid treatment. Treatment of diacids with thionyl chloride gave dicarboxylic acid dichlorides **13** and **14** in 94–98% yields (Scheme 2).

The cyclisation was carried out with fast addition of a mixture of the hydrazine monohydrochloride and triethylamine into a solution of dicarboxylic acid dichlorides **13** and **14** over 5 s with vigorous stirring at 0°C. Dihydrazide dilactams **4** and **5** were obtained in 60 and 50% yields respectively (Scheme 2). A low reaction time was observed for this macrocyclisation reaction. Our previous study[13,14] showed that CH_2Cl_2 is a properly selected solvent for this type macrocyclisation reaction.

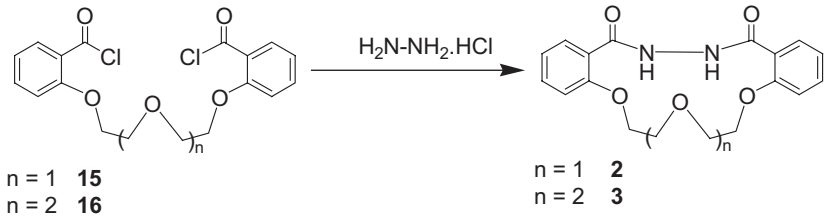
* Correspondent. E-mail: heshghi@ferdowsi.um.ac.ir

Low yields of the dihydrazide dilactam crown ethers in comparison with previously reported dilactam crown ethers can be attributed to the lower reactivity of hydrazine monohydrochloride which insoluble in organic solvent and can be converted to the hydrazine by triethylamine *in situ*. On the other hand, dicarboxylic acid dichlorides **13** and **14** are stable solid materials, due to two large naphthyl arms and thence with low reactivity. For examine this opinion we treated the previously prepared dicarboxylic acid dichlorides **15** and **16** with hydrazine monohydrochloride and triethylamine by the same procedure. Dihydrazide dilactams **2** and **3** were obtained in 80 and 65% yields respectively (Scheme 3). Increasing in the macrocyclisation yields suggested to the high reactivity of the dicarboxylic acid dichlorides **15** and **16** which recently cyclised successfully with different diamines to dilactam crown ethers in high yields under fast addition method.[13a,14]

Synthetic chemists continue to explore new methods to carry out chemical transformations.[15] In recent years, solvent-free reactions using either organic or inorganic solid supports have received increasing attention.[16,17] There are several advantages to performing synthesis in solvent free media:[15,18] (i) easy to isolate the products, (ii) short reaction times, (iii) increased safety, (iv) economic advantages due to the absence of solvent, (v) comparing the reaction conditions with those of related homogeneous reactions, they are so mild that a high yield of specific products and suppression of by-product formation are expected.[19] It is supposed in solvent free reactions; if the reaction between insoluble substrates in organic solvents is occurred that is an important advantage for solvent free conditions. So, macrocyclisation of the dicarboxylic acid dichlorides **13**–**16** with hydrazine monohydrochloride and triethylamine was examined in solvent-free conditions by simply grinding the mixture for 15 minutes. Unfortunately, in the cases of naphthalinoyl dichloride **13** and **14** the reaction failed and in the cases of the benzoyl dichlorides **15** and **16,** the corresponding dihydrazide **2** and **3** crown ethers were



Scheme 2



Scheme 3

obtained in moderate yields 50 and 42% respectively. Comparing the compounds **13–14** with **15–16** was shown that the former are solid, bulky and so unreactive than later which in these cases reactions were failed. We suggested that decreasing the yield in the cases of the dicarboxylic acid dichlorides **15** and **16** in solvent free conditions comparing with fast addition method can be due to several factors such as sensitivity of the acid chlorides to the moisture where the solvent free reactions were carried out usually in open vessels. Also, hydrazine, due to its low boiling point, is given off under these reaction conditions. So, the novel macrocyclic dihydrazides (**2–5**) which structurally related to luminol and would be applied as fluorescence sensors were readily obtained by fast addition method in moderate yields. The structures proposed for the macrocyclic compounds are consistent with data derived from IR, ^{1}H NMR and ^{13}C NMR in addition to satisfactory combustion analysis and molecular weights that determined by mass spectrometric analysis. The fluorescence behaviour of these compounds is under investigation.

Experimental

All materials and solvents were obtained from Merck chemical company (Germany) and Fluka (Switzerland). Melting points were determined in open capillary tubes in an Electrothermal IA 9000 melting point apparatus. IR spectra were recorded on a Shimadzu-IR 470 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker-500 MHz and Bruker-100 MHz instruments using tetramethylsilane (TMS) as an internal standard. Mass Spectra were determined on a Shimadzu GCMS-QP 1000 EX instrument at 70 eV. Elemental analyses were performed at the Research Institute of Petroleum Industry of Iran. Columns chromatography was carried out on short columns of silica gel 60 (230-400 mesh) in glass columns (2–3 cm diameter) using 15–30 g of silica gel per 1 g of crude mixture. Compounds **15** and **16** are known compounds and were prepared as previously described.[13a,14]

Preparation of diesters **9** *and* **10**

A mixture of dibromides (**7** or **8**) (0.1 mol) and 3-hydroxy-2-methylnaphthoate (**6**) (40.4 g, 0.2 mol) in acetone (500 ml) containing potassium carbonate (20 g) was refluxed for 7 days. The mixture was cooled, the solid was filtered and solvent evaporated. Chloroform (400 ml) was added, and the organic layer was washed with cold 10% aqueous sodium hydroxide solution (2 × 100 ml) and then with waters (2 × 100 ml) and was dried with anhydrous magnesium sulfate. The solvent was evaporated to give a yellow viscous oil of the corresponding diesters **9** and **10.**

Methyl-3-[2-(2-[3-(methoxycarbonyl)-2-naphthyl]oxyethoxy) ethoxy]-2-naphthoate (**9**): Yield 40.3 g (85%); IR (neat) 740 (s), 840 (m), 940 (m), 1062 (s), 1125 (s), 1200 (s), 1280 (s), 1330 (s), 1440 (s), 1490 (m), 1580 (s), 1620 (s), 1718 (s), 2920 (s), 3070 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.24 (s, 2H), 7.71 (d, 2H, *J* = 7.8 Hz), 7.61 (d, 2H, *J* = 7.9 Hz), 7.41 (t, 2H, *J* = 6.9 Hz), 7.28 (t, 2H, *J* = 7.3 Hz), 7.14 (s, 2H), 4.22 (m, 4H), 4.03 (m, 4H), 3.88 (s, 6H); ^{13}C NMR: 166.61, 154.83, 136.0, 132.63, 128.61, 128.30, 127.64, 126.50, 124.49, 122.22, 108.26, 69.88, 68.90, 52.06. MS *m/z* 474 (M^+, 15), 459 (5), 446 (10), 443 (15), 418 (20), 415 (5), 412 (12), 356 (35), 253 (23), 237 (25), 236 (14), 210 (12), 170, (10), 166 (14), 154 (26), 142 (16), 126 (base peak), 119 (45), 105 (25). Anal. Calcd. for $C_{28}H_{26}O_7$: C, 70.87; H, 5.52. Found: C, 70.5; H, 5.6.

Methyl-3-2-[2-(2-[3-(methoxycarbonyl)-2-naphthyl]oxyethoxy) ethoxy]ethoxy-2-naphthoate (**10**): Yield 41.4 g (80%); IR (neat) 760 (s), 870 (m), 950 (m), 1050 (s), 1120 (s), 1210 (s), 1305 (s), 1350 (s), 1420 (s), 1510 (m), 1595 (s), 1620 (s), 1730 (s), 2960 (s), 3070 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.29 (s, 2H), 7.79 (d, 2H, *J* = 10.0 Hz), 7.68 (d, 2H, *J* = 10.0 Hz), 7.48 (t, 2H, *J* = 7.5 Hz), 7.34 (t, 2H, *J* = 7.5 Hz), 7.2 (s, 2H), 4.29 (t, 4H, *J* = 5 Hz), 4.00 (t, 4H,

J = 5 Hz), 3.94 (s, 6H), 3.85 (s, 4H); ^{13}C NMR: 166.72, 154.87, 136.02, 132.7, 128.33, 128.65, 127.69, 126.50, 124.48, 122.21, 108.37, 71.18, 69.59, 68.81, 52.13. MS *m/z* 518 (M^+, 11), 503 (21), 490 (12), 487 (10), 462 (20), 459 (15), 456 (21), 400 (31), 274 (25), 237 (25), 210 (18), 170, (40), 166 (14), 154 (56), 142 (19), 126 (base peak), 119 (49), 105 (55). Anal. Calcd. for $C_{30}H_{30}O_8$: C, 69.49; H, 5.83. Found: C, 69.8; H, 5.9.

Preparation of diacids **11** *and* **12**

A solution of the diesters (**9** or **10**) (0.1 mol) in 10% aqueous NaOH (500 ml) was refluxed for 24 h. The mixture was cooled, washed with chloroform (2 × 100 ml), acidified with 6 N HCl, and extracted with CH_2Cl_2 (5 × 150 ml). The solvent was evaporated to give a yellow solid of the corresponding products.

3-(2-2-[(3-Carboxy-2-naphthyl)oxy]ethoxyethoxy)-2-naphthoic acid (**11**): Yield 43.7 g (98%); m.p. = 197–198°C; IR (neat) 760 (s), 830 (m), 920 (m), 1080 (s), 1120 (s), 1160, 1180, 1205 (s), 1290 (s), 1330 (s), 1440 (s), 1470 (m), 1500 (s), 1620 (s), 1705 (s), 2500–3200 (b) cm^{-1}; ^{1}H NMR (DMSO-d^6, 500 MHz) δ 12.84 (s, 2H), 8.24 (s, 2H), 7.94 (d, 2H, *J* = 8.1 Hz), 7.82 (d, 2H, *J* = 8.1 Hz), 7.53 (t, 2H, *J* = 7.1 Hz), 7.47 (s, 2H), 7.4 (t, 2H, *J* = 7.5 Hz), 4.30 (m, 4H), 3.98 (m, 4H); ^{13}C NMR: 167.37, 153.98, 135.27, 130.86, 128.36, 127.99, 127.27, 126.48, 124.37, 123.86, 108.01, 69.07, 68.46. MS *m/z* 446 (M^+, 10), 445 (M-1, 12), 444 (2), 429 (31), 410 (15), 401 (20), 356 (35), 253 (27), 237 (35), 236 (24), 210 (12), 170, (19), 166 (14), 154 (35), 142 (16), 126 (base peak), 119 (45). Anal. Calcd. for $C_{26}H_{22}O_7$: C, 69.95; H, 4.97. Found: C, 70.05; H, 5.2.

3-[2-(2-2-[(3-Carboxy-2-naphthyl)oxy]ethoxyethoxy)ethoxy]-2-naphthoic acid (**12**): Yield 48.0 g (98%); m.p. = 139–140°C; IR (neat) 760 (s), 850 (m), 940 (m), 1050 (s), 1120 (s), 1250 (s), 1290 (s), 1340 (s), 1450 (s), 1500 (s), 1620 (s), 1710 (s), 2500–3300 (b) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 11.80 (bs, 2H), 8.30 (s, 2H), 7.68 (d, 2H, *J* = 8.1 Hz), 7.62 (d, 2H, *J* = 8.1 Hz), 7.40 (t, 2H, *J* = 7.1 Hz), 7.27 (t, 2H, *J* = 7.5 Hz), 7.14 (s, 2H), 4.24 (m, 4H), 3.86 (m, 4H), 3.70 (s, 4H); ^{13}C NMR: 166.48, 153.74, 135.62, 133.15, 128.37, 128.22, 127.47, 126.16, 124.42, 120.76, 108.03, 70.31, 68.56, 68.37. MS *m/z* 490 (M^+, 12), 489 (M-1), (9), 488 (10), 473 (41), 454 (32), 445 (12), 400 (22), 253 (13), 237 (45), 236 (24), 210 (12), 170, (15), 166 (14), 154 (31), 142 (26), 126 (base peak), 121 (65), 119 (40), 105 (23), 91 (38). Anal. Calcd. for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 68.75; H, 5.2.

Preparation of diacid dichlorides **13** *and* **14**

The dicarboxylic acids (**11** or **12**) (0.025 mol) was heated in thionyl chloride (50 ml) for 12 h at 50–60°C. The thionyl chloride was evaporated at low temperature to give **13** and **14** as a white solid in 98% yields which applied in macrocyclisation step without additional purification.

3-(2-2-[(3-Chlorocarbonyl-2-naphthyl)oxy]ethoxyethoxy)-2-naphthalenecarbonyl chloride (**13**): IR (neat) 746 (s), 786 (s), 1109 (s), 1160 (s), 1242 (s), 1350 (m), 1450 (s), 1580 (s), 1630 (s), 1778 (s), 2880 (s), 3080 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 8.4 (s, 2H), 7.2–8.0 (m, 8H), 7.2 (s, 2 H), 4.2 (m, 4H), 3.9 (m, 4H).

3-[2-(2-2-[(3-Chlorocarbonyl-2-naphthyl)oxy]ethoxyethoxy)ethoxy]-2-naphthalenecarbonyl chloride (**14**): IR (neat) 750 (s), 850 (s), 950 (m), 1045 (s), 1128 (s), 1165 (s), 1185 (s), 1250 (s), 1290 (s),1350 (m), 1440 (s), 1480 (s), 1570 (s), 1600 (s), 1780 (s), 2900 (s), 3080 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 8.4 (s, 2H), 7.4–8.0 (m, 8H), 7.1 (s, 2 H), 4.2 (m, 4H), 3.8 (m, 4H), 3.4 (s, 4 H).

General procedure for the synthesis of dihydrazide dilactam crown ethers (**2–5**): A solution of hydrazine monohydrochloride (0.14 g, 2 mmol) and triethylamine (1.02 g, 10 mmol) in CH_2Cl_2 (5 ml) was added quickly (5 s) to a vigorously stirring solution of diacid chloride (**13–16**) (2 mmol) in CH_2Cl_2 (50 ml) at 0°C. The reaction mixture was stirred at room temperature for 20 mins. The precipitate was filtered off and the filtrate washed with water (2 × 50 ml) and 10% aqueous sodium hydroxide solution (50 ml) and then with water (100 ml). The organic layer was dried with anhydrous magnesium sulfate and the solvent was evaporated to give a solid (or oily) product. The crude product was purified by either recrystallisation from methylene chloride and n-hexane or column chromatography using petroleum ether (b.p. = 60–80°C)-ethyl acetate as eluent.

6,7,9,10,16,17,18,19-Octahydrodibenzo[h,n][1,4,7,11,12]trioxadiazacyclopentadecine-16,19-dione (**2**): Obtained in 80% yield; White solids; m.p. = 97–98°C; IR (KBr) 710 (s), 1092 (s), 1250 (s), 1532 (s), 1621 (s), 1651 (s), 2945 (s), 3090 (w), 3390 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.88 (br s, 2H, NH), 8.08 (dd, 2H, J_1 = 7.6 Hz, J_2 = 2.0 Hz), 7.51 (dt, 2H, J_1 = 7.5 Hz, J_2 = 1.5 Hz), 7.09 (t, 2H, *J* = 7.5 Hz), 7.03 (d, 2H, *J* = 8.0 Hz), 4.39 (m, 4H), 3.99 (m, 4H); ^{13}C NMR: 166.14, 157.40, 134.93, 133.47, 122.50, 118.48, 113.57, 69.05, 68.99; MS *m/z* 342 (M^+, 5), 340 (M-2, 25), 326 (10), 261 (3), 216 (15), 187 (30), 162 (95), 144 (54), 135 (90), 119 (base peak), 85 (98), 64 (65). Anal. Calcd. for $C_{18}H_{18}N_2O_5$: C, 63.15; H, 5.30; N, 8.18. Found: C, 62.95; H, 5.45; N, 8.35.

6,7,9,10,12,13,19,20,21,22-Decahydrodibenzo[k,q][1,4,7,10,14,15]tetraoxadiazacyclooctadecine-19,22-dione (**3**): Obtained in 65% yield; White solid; m.p. = 109–110°C; IR (KBr) 754 (s), 1047 (s), 1121 (s), 1237 (s), 1295 (s), 1446 (s), 1480 (s), 1536 (s), 1597 (s), 1648 (s), 2923 (s), 3080 (w), 3385 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.80 (br s, 2H, NH), 8.03 (dd, 2H, J_1 = 7.8 Hz, J_2 = 1.5 Hz), 7.48 (dt, 2H, J_1 = 7.5 Hz, J_2 = 1.5 Hz), 7.04 (t, 2H, *J* = 7.5 Hz), 7.00 (d, 2H, *J* = 8.0 Hz), 4.32 (t, 4H, *J* = 4.5 Hz), 3.88 (t, 4H, *J* = 4.5 Hz), 3.71 (s, 4H); ^{13}C NMR: 166.68, 158.32, 133.37, 131.55, 120.70, 120.52, 113.81, 70.64, 69.54, 68.94; MS *m/z* 386 (M^+, 3), 384 (M-2, 40), 339 (3), 261 (8), 229 (10), 204 (11), 186 (35), 161 (70), 143 (55), 135 (20), 118 (base peak), 102 (25), 90 (55), 63 (55). Anal. Calcd. for $C_{20}H_{22}N_2O_6$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.35; H, 5.45; N, 7.35.

7,8,10,11,19,20,21,22-Octahydrodinaphtho[2,3-h: 2,3-n][1,4,7,11,12]trioxadiazacyclopentadecine-19,22-dione (**4**): Obtained in 60% yield; yellow solid; m.p. = 180–181°C; IR (KBr) 741 (s), 1096 (s), 1129 (s), 1223 (s), 1354 (s), 1444 (s), 1498 (s), 1537 (s), 1594 (s), 1643 (s), 2925 (s), 3056 (w), 3270 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.30 (br s, 2H, NH), 8.42 (s, 2H), 7.75 (d, 2H, *J* = 8.2 Hz), 7.63 (d, 2H, *J* = 8.3 Hz), 7.45 (t, 2H, *J* = 7.5 Hz), 7.28 (t, 2H, *J* = 7.8 Hz), 7.26 (s, 2H), 3.78 (t, 4H, *J* = 6.2 Hz), 3.45 (t, 4H, *J* = 6.2 Hz); ^{13}C NMR: 170.09, 156.16, 137.74, 132.31, 129.13, 129.08, 126.88, 126.14, 123.85, 114.04, 111.47, 71.12, 70.38. MS *m/z* 442 (M^+, 12), 440 (M-2, 25), 414 (31), 399 (10), 253 (3), 237 (5), 210 (12), 166 (4), 165 (38), 147 (36), 121 (base peak), 119 (40), 105 (22), 92 (30), 91 (38), 76 (18). Anal. Calcd. for $C_{26}H_{22}N_2O_5$: C, 70.58; H, 5.01; N, 6.33. Found: C, 70.65; H, 5.35; N, 6.35.

7,8,10,11,13,14,22,23,24,25-Decahydrodinaphtho[2,3-k: 2,3-q][1,4,7,10,14,15]tetraoxadiazacyclooctadecine-22,25-dione (**5**): Obtained in 50% yield; yellow solids; m.p. = 185–186°C; IR (KBr) 754 (s), 928 (s), 1043 (s), 1126 (s), 1158(s), 1237 (s), 1296 (s), 1446 (s), 1480 (s), 1537 (s), 1597 (s), 1645 (s), 2935 (s), 3070 (w), 3390 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.39 (br s, 2H, NH), 8.33 (s, 2H), 7.68 (d, 2H, *J* = 8.2 Hz), 7.58 (d, 2H, *J* = 8.3 Hz), 7.40 (t, 2H, *J* = 7.5 Hz), 7.23 (t, 2H, *J* = 7.5 Hz), 7.22 (s, 2H), 3.89 (s, 4H), 3.72 (t, 4H, *J* = 6.2 Hz), 3.39 (t, 4H, *J* = 6.2 Hz); ^{13}C NMR: 170.10, 156.19, 137.75, 132.29, 129.13, 129.04, 126.88, 126.14, 123.81, 114.01, 111.48, 70.86, 70.44, 70.13. MS *m/z* 486 (M^+, 10), 484 (M-2, 35), 442 (31), 253 (13), 237 (15), 210 (22), 166 (14), 165 (38), 147 (39), 122 (base peak), 119 (40), 105 (22), 92 (60), 91 (45), 76 (28). Anal. Calcd. for $C_{28}H_{26}N_2O_6$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.29; H, 5.45; N, 5.95.

General procedure for the solvent-free synthesis of dihydrazide dilactam crown ethers (**2** *and* **3**)

A mixture of hydrazinemonohydrochloride (0.14 g, 2 mmol), triethylamine (0.61 g, 6 mmol), and diacid chloride (**15** or **16**) (2 mmol) was grinded in a mortar and pestle for 10 min. The reaction mixture was treated with water (20 ml) and extracted with dichloromethane (2 × 20 ml). The organic layer was washed with water (2 × 20 ml) and 10% aqueous sodium hydroxide solution (20 ml) and then with water (30 ml). The organic layer was dried with anhydrous magnesium sulfate and the solvent was evaporated to give a solid product. The crude product was purified by either recrystallisation from methylene chloride and *n*-hexane or column chromatography using petroleum ether (b.p. = 60–80°C)-ethyl acetate as eluent. Compounds **2** and **3** were obtained by this procedure in 50 and 42% yields respectively, with the same characterisation as reported above in fast addition procedure.

We thank Sistan and Baluchestan University for the partial support of this work.

Received 30 July 2006; accepted 3 October 2006
Paper 06/4107

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