A Facile and Convenient Method for the Preparation of Macrocyclic Diamides

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A number of macrocyclic diamides have been synthesized from the reaction of a diacid dicarboxylic dichloride with primary diamino compound in the presence of magnesium oxide-silica gel at room temperature in good yields. Using urea and thiourea as well as diamines to produce the corresponding macrocycles in the range of 52-56% yields are also included in this paper. One of the major advantages of this method is simple regeneration of inorganic solid and its reuse through several cycles without a decrease in activity.

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Introduction.

There is continuing interest in the preparation of macrocyclic diamides which have important uses in selective noble metals complexing [1-3] and metal ion selective electrode [4,5] as well as being valuable intermediates for the synthesis of azacrowns and related compounds [6-10]. Published methods for the preparation of macrocyclic diamides include the following. Carboxylic acid derivatives, such as malonic and α,ω-dicarboxylic acid esters [11]. Labile diacid dichlorides [10,12], and bis(α-chloroamide) compounds [6-9], were allowed to react with various diamines under high dilution or for long reaction periods. Controlled and specific conditions such as simultaneous addition of two reactants through syringe pumps at reflux were used to avoid undesired side reactions [6]. With regard to the procedures for the synthesis of macrocyclic diamides, Shanzer [13] used silicon as a covalent template to prepare macrocyclic amides in 12-40% yields. Some benzo-substituted macrocyclic diamides have been synthesized by the reaction of 1,2-bis(2-hydroxybenzoylamino)alkyl or aryl derivatives with dichloro or dibromo compounds [14,15]. Fujita and co-workers [16] monitored the amide ring formation by aminolysis of 3-acylthiazolidine-2-thione. This method generally gave satisfactory yields, yet was handicapped by the use of toxic thallium salts and labile acid dichlorides. Moreover, besides the desired one-to-one adduct, two-to-two cyclization products were sometimes obtained [8,16], which increased the problems of purification. Recently, we reported an efficient procedure to synthesize macrocyclic diamides [17]. Although this method was simple, it had some problems. On the other hand, hydrogen chloride evolution caused environmental problems during the reaction, and also in some cases two-to-two condensation products were found.

Reaction under dry conditions (*i.e.* in the absence of a solvent, on a solid support with or without catalysts) were originally developed in recent years [18]. Many interesting reactions were investigated in the presence of inorganic solids such as alumina [19-22], clay [23], and silica gel [24]. The notable advantages for most of these reactions are operational simplicity, generality, excellent regioselectivity, no side reactions, and quantitative yields.

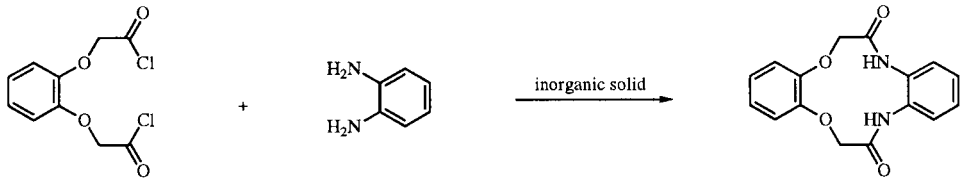
Having the above facts in mind, we wish to report a convenient method for preparing macrocyclic diamides from the reaction of diamine with diacid dicarboxylic dichloride in dry media. Using urea and thiourea in place of a diamine are also included in this paper.

Results and Discussion.

The synthesis began by simply mixing a diamine with an inorganic solid and then adding diacid dicarboxylic dichloride and stirring at room temperature for 2 hours. Then, methanol was added and the inorganic solid was filtered. The solvent was evaporated and the crude product was purified by chromatography on a short column of silica gel to separate macrocyclic diamide from unreacted starting materials. The inorganic solid was easily regenerated and could be reused several times.

In order to evaluate cyclization conditions, we prepared model compound **5** as shown in Scheme 1. In a preliminary study, the effect of some inorganic solids on the yield of the macrocyclization reaction was investigated with the formation of dilactam **5** as the model reaction (Table 1). Table 1, clearly indicated, magnesium oxide-silica gel is the best solid for this macrocyclization reaction. In an effort to evaluate the range of applicability of our method, we examined also some other diacid dicarboxylic dichlorides and diamines in the presence of magnesium oxide-silica gel (Schemes 2, 3). At first, the reaction of diamino compound **2** was investigated with various types of diacid dicarboxylic dichlorides. As shown in Scheme 2, several types of aromatic and aliphatic solid or liquid diacid dicarboxylic dichlorides reacted with diamino compound **2** in the presence of magnesium oxide-silica gel to afford macrocyclic diamides in the range of 51-70% yields (Table 2, entries 2-6).

Scheme 1



(1) (5)

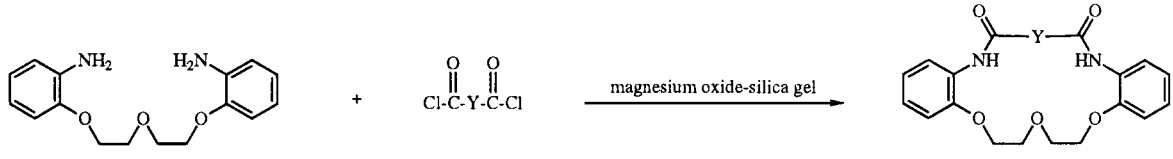
Table 1

Effect of Inorganic Solids in Macrocyclization Yield (%) Between Compound **1** and Phenylene Diamine

Inorganic Solid	Time (hours)	Yield(%) [a]
Silica gel	3	35
Al_2O_3-basic	3	43
Al_2O_3-basic/Silica gel	2	44
$CuSO_4$	3	26
K_2CO_3	4	44
CaO	3	31
MgO	2	49
MgO/Silica gel	2	52

[a] Isolated yield.

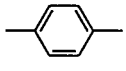
Scheme 2

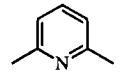


(2) (6-10)

Y = — (6)

Y = $(CH_2)_4$ (7)

Y =  (8)

Y =  (9)

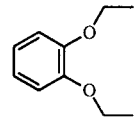
Y =  (10)

Table 2

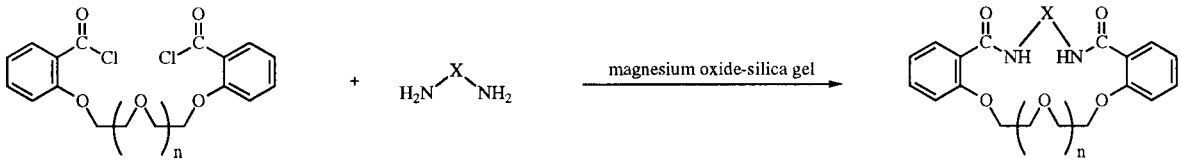
Cyclization Yields and ^1H NMR Spectra of Macrocyclic Diamides **5-20**

Entry	Compound	Yield (%)	^1H NMR Spectra (90 or 250 MHz, $CDCl_3$ or d_6-acetone, δ) [b]
1	**5**	52	4.70 (s, 4H), 6.99 (dd, 2H, J_1= 7.15 Hz, J_2 = 2.55 Hz), 7.23 (dt, 4H, J_1 = 5.65 Hz, J_2 = 2.00 Hz), 7.64 (dd, 2H, J_1 = 9.90 Hz, J_2 = 2.50 Hz), 9.27 (b, 2H).
2	**6**	60	3.75 (t, 4H, J = 4.50 Hz), 4.10 (t, 4H, J = 4.50 Hz), 6.70-7.50 (complex, 8H), 8.25 (b, 2H).
3	**7**	70	1.85 (t, 4H, J = 4.80 Hz), 2.35 (t, 4H, J = 4.80 Hz), 3.90 (t, 4H, J = 4.50 Hz), 4.20 (t, 4H, J = 4.50 Hz), 6.60-7.00 (complex, 6H), 8.15 (dd, 2H, J_1 = 8.00 Hz, J_2 = 2.00 Hz), 8.25 (b, 2H).
4	**8**	51	3.40 (t, 4H, J = 4.50 Hz), 3.55 (t, 4H, J = 4.50 Hz), 6.70-7.10 (complex, 6H), 7.40 (s, 4H), 7.50 (dd, 2H, J_1 = 7.00 Hz, J_2 = 2.00 Hz), 9.15 (b, 2H).
5	**9**	51	3.86 (t, 4H, J = 4.00 Hz), 4.20 (t, 4H, J = 4.00 Hz), 6.80 (dd, 2H, J_1 = 7.85 Hz, J_2 = 1.75 Hz), 6.94 (dt, 2H, J_1 = 7.75 Hz, J_2 = 1.75 Hz), 7.08 (dt, 2H, J_1 = 7.70 Hz, J_2 = 1.80 Hz), 8.00 (t, 1H, J = 6.35 Hz), 8.18 (dd, 2H, J_1 = 7.80 Hz, J_2 = 1.80 Hz) 8.47 (dd, 2H, J_1 = 7.80 Hz, J_2 = 1.65 Hz), 9.64 (s, 2H).
6	**10**	51	3.65 (t, 4H, J = 4.50 Hz), 3.98 (t, 4H, J = 4.50 Hz), 4.53 (d, 4H, J = 2.50 Hz), 6.72 (dd, 2H, J_1 = 7.50 Hz, J_2 = 2.00 Hz), 6.80-6.90 (complex, 8H), 8.23 (dd, 2H, J_1 = 7.60 Hz, J_2 = 2.00 Hz), 9.02 (b, 2H).
7	**11**	50	1.55 (m, 8H), 3.40 (m, 4H), 3.90 (t, 4H, J = 4.00 Hz), 4.20 (t, 4H, J = 4.00 Hz), 7.00 (complex, 4H), 7.25 (dt, 2H, J_1 = 8.00 Hz, J_2 = 2.00 Hz), 8.00 (b, 2H), 8.05 (dd, 2H, J_1 = 8.00 Hz, J_2 = 2.00 Hz).
8	**12**	53	1.43-1.58 (m, 8H), 3.38 (t, 4H, J = 6.00 Hz), 3.65 (s, 4H), 3.83 (t, 4H, J = 4.25 Hz), 4.17 (t, 4H, J = 4.25 Hz), 6.83 (dd, 2H, J_1 = 8.25 Hz, J_2 = 0.75 Hz), 7.01 (dt, 2H, J_1 = 7.55 Hz, J_2 = 0.75 Hz), 7.31 (dt, 2H, J_1 = 7.80 Hz, J_2 = 0.75 Hz), 7.97 (b, 2H), 8.13 (dd, 2H, J_1 = 7.85 Hz, J_2 = 0.75 Hz).
9	**13**	54	3.35 (s, 4H), 3.56 (t, 4H, J = 4.00 Hz), 4.01 (t, 4H, J = 4.00 Hz), 6.83 (dd, 2H, J_1 = 7.50 Hz, J_2 = 1.50 Hz), 6.98 (dt, 2H, J_1 = 7.50 Hz, J_2 = 1.50 Hz), 7.13 (dt, 2H, J_1 = 7.80 Hz, J_2 = 2.40 Hz), 7.30 (dt, 2H, J_1 = 7.75 Hz, J_2 = 1.75 Hz), 7.82 (dd, 2H, J_1 = 7.30 Hz, J_2 = 2.40 Hz), 7.94 (dd, 2H, J_1 = 7.50 Hz, J_2 = 1.75 Hz), 9.57 (s, 2H).
10	**14**	56	3.66 (t, 4H, J = 4.00 Hz), 4.23 (t, 4H, J = 4.00 Hz), 6.90 (dd, 2H, J_1 = 8.25 Hz, J_2 = 0.5 Hz), 7.07 (dt, 2H, J_1 = 7.25 Hz, J_2 = 1.00 Hz), 7.43 (dt, 2H, J_1 = 7.75 Hz, J_2 = 1.75 Hz), 7.76 (dd, 2H, J_1 = 7.75 Hz, J_2 = 1.75 Hz), 12.37 (b, 2H).
11	**15**	52	3.52 (s, 4H), 3.76 (t, 4H, J = 5.00 Hz), 4.33 (t, 4H, J = 5.00 Hz), 6.97 (dd, 2H, J_1 = 8.25 Hz, J_2 = 0.5 Hz), 7.06 (dt, 2H, J_1 = 7.25 Hz, J_2 = 1.00 Hz), 7.48 (dt, 2H, J_1 = 7.75 Hz, J_2 = 1.75 Hz), 7.79 (dd, 2H, J_1 = 8.00 Hz, J_2 = 1.75 Hz), 12.35 (d, 2H).
12	**16**	55	3.83 (t, 4H, J = 4.50 Hz), 4.16 (t, 4H, J = 4.50 Hz), 6.86 (dd, 2H, J_1 = 8.25 Hz, J_2 = 0.75 Hz), 7.01 (dt, 2H, J_1 = 7.50 Hz, J_2 = 0.75 Hz), 7.37 (dt, 2H, J_1 = 7.80 Hz, J_2 = 1.80 Hz), 7.89 (dd, 2H, J_1 = 7.80 Hz, J_2 = 1.80 Hz), 9.15 (b, 2H).
13	**17**	52	3.77 (s, 4H), 3.88 (t, 4H, J = 5.00 Hz), 4.15 (t, 4H, J = 5.00 Hz), 6.83 (dd, 2H, J_1 = 8.00 Hz, J_2 = 0.75 Hz), 6.87 (dt, 2H, J_1 = 7.50 Hz, J_2 = 0.75 Hz), 7.29 (dt, 2H, J_1 = 7.85 Hz, J_2 = 1.75 Hz), 7.65 (dd, 2H, J_1 = 7.75 Hz, J_2 = 1.75 Hz), 9.05 (b, 2H).
14	**18**	20	3.53 (t, 8H, J = 5.00 Hz), 3.59 (s, 4H), 3.74 (s, 4H), 3.86 (t, 4H, J = 5.00 Hz), 4.16 (t, 4H, J = 5.00 Hz), 6.83 (dd, 2H, J_1 = 7.50 Hz, J_2 = 0.75 Hz), 6.99 (dt, 2H, J_1 = 7.50 Hz), J_2 = 0.75 Hz), 7.32 (dt, 2H, J_1 = 7.50 Hz, J_2 = 2.50 Hz), 8.11 (dd, 2H, J_1 = 7.50 Hz, J_2 = 2.50 Hz), 8.35 (b, 2H).
15	**19**	15	3.72 (s, 4H), 3.74 (s, 4H), 3.86 (t, 4H, J = 4.50 Hz), 4.21 (t, 4H, J = 4.50 Hz), 6.91 (dd, 2H, J_1 = 8.00 Hz, J_2 = 0.75 Hz), 7.05 (dt, 2H, J_1 = 7.50 Hz, J_2 = 0.75 Hz) 7.37 (dt, 2H, J_1 = 7.60 Hz, J_2 = 1.75 Hz), 8.09 (dd, 2H, J_1 = 7.80 Hz, J_2 = 1.75 Hz), 8.20 (b, 2H).
16	**20**	18	1.45 (t, 1H), 3.0 (dt, 4H, J_1 = 4.50 Hz, J_2 = 2.00 Hz), 3.70 (t, 4H, J = 4.50 Hz), 3.90 (dt, 4H, J_1 = 4.50 Hz, J_2 = 2.00 Hz), 4.10 (t, 4H, J = 4.50 Hz), 6.80 (d, 2H, J = 8.00 Hz), 7.00 (t, 2H, J = 7.00 Hz), 7.20 (dt, 2H, J_1 = 8.00 Hz, J_2 = 2.00 Hz), 8.00 (dd, 2H, J_1 = 8.00 Hz, J_2 = 2.00 Hz), 8.50 (b, 2H).

[b] 90 MHz for **6-8**, **11**, **20**; 250 MHz for **5**, **9**, **10**, **12-19**.

Subsequently, the reactions of diacid dicarboxylic dichlorides **3**, **4** were investigated with different diamino compounds. As shown in Scheme 3, diacid dicarboxylic dichlorides, **3**, **4** gave the corresponding macrocyclic diamides in the range of 50-54% yields with solid aromatic and aliphatic diamines (Table 2, entries 7-9), and low yields in the case of liquid diamines (Table 2, entries 14-16). While we were not satisfied with the yield obtained in this case, variation of adding starting materials, increasing temperature to 60° and reaction time even

Scheme 3



n = 1 (**3**)
n = 2 (**4**)

(**11-20**)

X = $(CH_2)_6$ n = 1 (**11**)
n = 2 (**12**)

X =  n = 2 (**13**)

X =  n = 1 (**14**)
n = 2 (**15**)

X =  n = 1 (**16**)
n = 2 (**17**)

X = $(CH_2)_2O(CH_2)_2O(CH_2)_2$ n = 2 (**18**)

X = $(CH_2)_2$ n = 2 (**19**)

X = $(CH_2)_2NH(CH_2)_2$ n = 1 (**20**)

to 24 hours failed to improve the amount of product obtained. In part, this fact could mean that adsorption of a liquid diamine on the surface of an inorganic solid reduces its reactivity towards a diacid dicarboxylic dichloride. As shown in Scheme 3, an additional point of interest of our described procedure is presented by the possibility of using urea and thiourea as well as diamines to produce the corresponding macrocycles in the range of 52-56% yields (Table 2, entries 10-13).

In conclusion, the current method provides a very simple and convenient procedure for the synthesis of macrocyclic diamides. In addition, we have been developing a simple and economical method for preparing macrocyclic diamides that occurs under mild conditions using inexpensive inorganic solids. Moreover, synthetic versatility, no side reactions, no hydrogen chloride evolution, ease of workup, regenerability of inorganic solid, and short reaction time can be considered as the advantages of this method.

EXPERIMENTAL

Instrumentation, Analyses and Starting Material.

The nmr spectra were recorded using either a Bruker Avance DPX-250 or a Varian EM 390 (90 MHz) spectrometer in pure deuterated solvents. The ir spectra were obtained on an Impact 400 D Nickolet FTIR spectrometer. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instrument at 20 or 70 eV. Thin layer chromatography (tlc) analyses were performed with silica gel polygram SILG/UV 254 plates. Elemental analyses were performed at the National Oil Co. of Iran, Tehran Research Center. Column 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. Melting points were determined in open capillary tubes in a Buchi-510 circulating oil melting point apparatus. Inorganic solids magnesium oxide, potassium carbonate, cupric sulfate, basic alumina (70-230 mesh), silica gel (60-120 mesh) and other chemical materials were purchased from Merck, Fluka, BDH and Aldrich in high purity and were used without further purification. Compounds **1** [25], **2** [26], **3**,**4** [27] were prepared according to their published procedures and their spectroscopic and physical data were compared with the literature data.

General Procedure for the Synthesis of Macrocyclic Diamides.

A mixture of diamine (1 mmole), silica gel [60-120 mesh] (0.5 g), magnesium oxide (0.5 g) and diacid dicarboxylic dichloride (1 mmole) was ground in a mortar and then placed in a round-bottomed flask and magnetically stirred at room temperature. After 2 hours, methanol (20 ml) was added and magnesium oxide-silica gel was filtered and thoroughly washed with methanol (30 ml). Evaporation of methanol gave a solid (or oily) product. The crude product was purified by column chromatography using petroleum ether (bp = 60-80°)-ethyl acetate as the eluent. The macrocycles **6-8** [26], **14**, **15** [27], **11**, **20** [17], are known compounds, and their spectroscopic and physical data were compared with the literature data.

1,4-Diaza-2,3;8,9-dibenzo-7,10-dioxacyclododecane-5,12-dione (**5**).

This compound is a white solid, mp 213-214°; ir (potassium bromide): 623 (w), 692 (w), 731 (m), 1027 (w), 1035 (w), 1105 (m), 1123 (w), 1188 (m), 1255 (m), 1290 (w), 1445 (m), 1490 (s), 1590 (m), 1668 (s), 2850 (w), 2913 (m), 3030 (w), 3301 (s) cm^{-1}; ^1H nmr (perdeuterioacetone, 250 MHz): δ 4.70 (s, 4H),

6.99 (dd, 2H, J_1 = 7.15 Hz, J_2 = 2.55 Hz), 7.23 (dt, 4H, J_1 = 5.65 Hz, J_2 = 2.00 Hz), 7.64 (dd, 2H, J_1 = 9.90 Hz, J_2 = 2.50 Hz), 9.27 (b, 2H); ms: m/z 300 (M^++2, 0.3), 299 (M^++1, 2.6), 298 (M^+, 12.7), 176 (3.5), 175 (28.5), 148 (10.1), 147 (44.8), 137 (6.2), 134 (82.8), 133 (10), 132 (13.4), 121 (25.2), 120 (13.9), 119 (base peak), 118 (6.6), 106 (13.8), 105 (12), 92 (16.6), 91 (5.4), 77 (19.8).

Anal. Calcd. for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.51; H, 4.66; N, 9.42.

3,15,21-Triaza-4,5;13,14-dibenzo-6,9,12-trioxabicyclo[15.3.1]-uneicosa-1(21),17,19-triene-2,16-dione (**9**).

This compound is white crystals, mp 223-224°; ir (potassium bromide): 625 (w), 740 (s), 930 (m), 989 (m), 1058 (m), 1101 (m), 1132 (m), 1203 (m), 1250 (s), 1319 (m), 1438 (m), 1478 (m), 1512 (s), 1594 (s), 1675 (s), 2880 (m), 2930 (m), 3090 (w), 3395 (s) cm^{-1}; ^1H nmr (deuteriochloroform, 250 MHz): δ 3.86 (t, 4H, J = 4.00 Hz), 4.20 (t, 4H, J = 4.00 Hz), 6.80 (dd, 2H, J_1 = 7.85 Hz, J_2 = 1.75 Hz), 6.94 (dt, 2H, J_1 = 7.75 Hz, J_2 = 1.75 Hz), 7.08 (dt, 2H, J_1 = 7.70 Hz, J_2 = 1.80 Hz), 8.00 (t, 1H, J = 6.35 Hz), 8.18 (dd, 2H, J_1 = 7.80 Hz, J_2 = 1.80 Hz), 8.47 (dd, 2H, J_1 = 7.80 Hz, J_2 = 1.65 Hz), 9.64 (s, 2H); ms: m/z 421 (M^++2, 5.5), 420 (M^++1, 29.8), 419 (M^+, base peak), 376 (6.2), 375 (12.3), 331 (4.1), 314 (3.1), 303 (4.1), 302 (1.4), 286 (3.5), 273 (1.5), 272 (6.2), 258 (2.8), 223 (6.6), 196 (13.4), 135 (8.9), 134 (77.9), 107 (18.2), 93 (3.9), 91 (1.1), 71 (2.2).

Anal. Calcd. for $C_{23}H_{21}N_3O_5$: C, 65.86; H, 5.05; N, 10.02. Found: C, 65.73; H, 5.13; N, 9.92.

1,13-Diaza-2,3;11,12;17,18-tribenzo-4,7,10,16,19-pentaoxacyclo-uneicosane-14,21-dione (**10**).

This compound is a white solid, mp 183-185°; ir (potassium bromide): 744.5 (m), 930.6 (w), 1033 (w), 1050 (w), 1112 (m), 1133 (w), 1210 (w), 1253 (m), 1287 (w), 1337 (w), 1448 (m), 1489 (m), 1532 (s), 1600 (m), 1682 (s), 2883 (m), 2910 (m), 3030 (w), 3382 (s) cm^{-1}; ^1H nmr (deuteriochloroform, 250 MHz): δ 3.65 (t, 4H, J = 4.50 Hz), 3.98 (t, 4H, J = 4.50 Hz), 4.53 (d, 4H, J = 2.50 Hz), 6.72 (dd, 2H, J_1 = 7.50 Hz, J_2 = 2.00 Hz), 6.80-6.90 (complex, 8H), 8.23 (dd, 2H, J_1 = 7.60 Hz, J_2 = 2.00 Hz), 9.02 (b, 2H); ms: m/z 480 (M^++2, 2.6), 479 (M^++1, 10), 478 (M^+, 28.9), 435 (12.6), 434 (43.8), 315 (2.9), 298 (4.2), 270 (5), 223 (5.7), 191 (3.2), 167 (11.6), 154 (10.5), 149 (43.5), 148 (75), 137 (35.9), 136 (46.4), 135 (67.5), 134 (32.5), 122 (46.2), 121 (40.4), 120 (base peak), 109 (57.8), 108 (23.1), 107 (14.4), 95 (16.2), 93 (11.5), 91 (6.8), 77 (11.3), 71 (15).

Anal. Calcd. for $C_{26}H_{26}N_2O_7$: C, 65.26; H, 5.48; N, 5.85. Found: C, 65.15; H, 5.54; N, 5.81.

1,18-Diaza-3,4;15,16-dibenzo-5,8,11,14-tetraoxacyclotetraeicosane-2,17-dione (**12**).

This compound is white crystals, mp 182-184°; ir (potassium bromide): 601.5 (m), 749.3 (m), 878.6 (w), 928.6 (m), 1044.8 (m), 1114.3 (m), 1239.6 (s), 1293 (m), 1442.3 (w), 1485.7 (m), 1541.8 (s), 1590 (m), 1635.8 (s), 2851.5 (m), 2925.4 (s), 3059.7 (w), 3335.7 (s), 3388.8 (s) cm^{-1}; ^1H nmr (deuteriochloroform, 250 MHz): δ 1.43-1.58 (m, 8H), 3.38 (t, 4H, J = 6.00 Hz), 3.65 (s, 4H), 3.83 (t, 4H, J = 4.25 Hz), 4.17 (t, 4H, J = 4.25 Hz), 6.83 (dd, 2H, J_1 = 8.25 Hz, J_2 = 0.75 Hz), 7.01 (dt, 2H, J_1 = 7.55 Hz, J_2 = 0.75 Hz), 7.31 (dt, 2H, J_1 = 7.80 Hz, J_2 = 0.75 Hz), 7.97 (b, 2H), 8.13 (dd, 2H, J_1 = 7.85 Hz, J_2 = 0.75 Hz); ms: m/z 472 (M^++2, 12.1), 471 (M^++1, 45.3), 470 (M^+, 53.8), 442 (5.8), 427 (7.9), 398 (6.8), 374 (38), 349 (19.5), 332 (12.9), 306 (17.9), 266 (12.1), 235 (21.4), 232 (21.8), 209 (23.3), 190 (23.3), 165 (61.3), 147 (25.4), 121 (64), 98 (71.3), 97 (base peak), 96 (15), 91 (8.1), 73 (19.1), 70 (24.5).

Anal. Calcd. for $C_{26}H_{34}N_2O_6$: C, 66.37; H, 7.28; N, 5.95. Found: C, 66.19; H, 7.32; N, 6.03.

1,18-Diaza-3,4;15,16;19,20-tribenzo-5,8,11,14-tetraoxacycloeicosane-2,17-dione (**13**).

This compound is white crystals, mp 180-182°; ir (potassium bromide): 690 (m), 755 (s), 930 (m), 1015 (m), 1125 (s), 1205 (m), 1306 (s), 1350 (m), 1475 (m), 1535 (s), 1600 (m), 1662 (s), 2898 (m), 3060 (w), 3265 (m), 3314 (s) cm^{-1}; ^1H nmr (deuteriochloroform, 250 MHz): δ 3.35 (s, 4H), 3.56 (t, 4H, J = 4.00 Hz), 4.01 (t, 4H, J = 4.00 Hz), 6.83 (dd, 2H, J_1 = 7.50 Hz, J_2 = 1.50 Hz), 6.98 (dt, 2H, J_1 = 7.50 Hz, J_2 = 1.50 Hz), 7.13 (dt, 2H, J_1 = 7.80 Hz, J_2 = 2.40 Hz), 7.30 (dt, 2H, J_1 = 7.75 Hz, J_2 = 1.75 Hz), 7.82 (dd, 2H, J_1 = 7.30 Hz, J_2 = 2.40 Hz), 7.94 (dd, 2H, J_1 = 7.50 Hz, J_2 = 1.75 Hz), 9.57 (s, 2H); ms: m/z 464 (M^++2, 28.9), 463 (M^++1, base peak), 462 (M^+, 61.7), 445 (6.7), 325 (13.9), 237 (12.3), 210 (15.3), 165 (16.9), 147 (10.9), 121 (24.1), 119 (13.4), 73 (7.4).

Anal. Calcd. for $C_{26}H_{26}N_2O_6$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.65; H, 5.71; N, 5.93.

1,15-Diaza-3,4;12,13-dibenzo-5,8,11-trioxacyclohexadecane-2,15,16-trione (**16**).

This compound is an oil, bp = 248-250° dec; ir (neat): 687.8 (w), 756 (s), 930 (w), 1045 (m), 1140 (m), 1246.3 (s), 1305 (m), 1372 (w), 1471 (s), 1486 (m), 1602.2 (m), 1723.1 (s), 2886 (w), 2925.4 (m), 3014 (w), 3086 (w), 3274.6 (m) cm^{-1}; ^1H nmr (deuteriochloroform, 250 MHz): δ 3.83 (t, 4H, J = 4.50 Hz), 4.16 (t, 4H, J = 4.50 Hz), 6.86 (dd, 2H, J_1 = 8.25 Hz, J_2 = 0.75 Hz), 7.01 (dt, 2H, J_1 = 7.50 Hz, J_2 = 0.75 Hz), 7.37 (dt, 2H, J_1 = 7.80 Hz, J_2 = 1.80 Hz), 7.89 (dd, 2H, J_1 = 7.80 Hz, J_2 = 1.80 Hz), 9.15 (b, 2H); ms: m/z 328 (3.4), 327 (M^+-HNCO, 2.8), 284 (1.9), 239 (4.8), 208 (1.8), 183 (3.7), 165 (30), 164 (11.5), 138 (8), 121 (base peak), 120 (32.1), 105 (4.9), 92 (19.1), 77 (8.9).

Anal. Calcd. for $C_{19}H_{18}N_2O_6$: C, 61.62; H, 4.90; N, 7.56. Found: C, 61.76; H, 4.81; N, 7.45.

1,18-Diaza-3,4;15,16-dibenzo-5,8,11,14-tetraoxacyclononadecane-2,17,19-trione (**17**).

This compound is an oil, bp = 248-250° dec; ir (neat): 670 (w), 705 (w), 756 (s), 930 (w), 960 (w), 1055 (m), 1085 (s), 1140 (m), 1246.3 (s), 1303 (s), 1447.8 (s), 1490 (m), 1602.2 (m), 1723.1 (s), 2871.6 (m), 2938.8 (m), 3086 (w), 3274.6 (m) cm^{-1}; ^1H nmr (deuteriochloroform, 250 MHz): δ 3.77 (s, 4H), 3.88 (t, 4H, J = 5.00 Hz), 4.15 (t, 4H, J = 5.00 Hz), 6.83 (dd, 2H, J_1 = 8.00 Hz, J_2 = 0.75 Hz), 6.87 (dt, 2H, J_1 = 7.50 Hz, J_2 = 0.75 Hz), 7.29 (dt, 2H, J_1 = 7.85 Hz, J_2 = 1.75 Hz), 7.65 (dd, 2H, J_1 = 7.75 Hz, J_2 = 1.75 Hz), 9.05 (b, 2H); ms: m/z 387 (M^+-CO, 8.3), 223 (12.2), 191 (2.2), 179 (69.4), 178 (11.2), 165 (20), 152 (25.4), 147 (13.8), 121 (base peak), 120 (30.4), 105 (4.7), 92 (21), 77 (13.3), 73 (11.3).

Anal. Calcd. for $C_{21}H_{22}N_2O_7$: C, 60.86; H, 5.35; N, 6.76. Found: C, 60.59; H, 5.49; N, 6.91.

1,18-Diaza-3,4;15,16-dibenzo-5,8,11,14,21,24-hexaoxacyclohexacicosane-2,17-dione (**18**).

This compound is white crystals, mp 111-113°; ir (potassium bromide): 613 (w), 756 (m), 930.6 (w), 1033 (w), 1105.2 (m),

1103 (m), 1233 (m), 1306.7 (m), 1330 (w), 1437 (w), 1488 (m), 1541.8 (s), 1593 (w), 1649.2 (s), 2878.3 (m), 2933 (m), 3030 (w), 3375.3 (s) cm^{-1}; ^1H nmr (deuteriochloroform, 250 MHz): δ 3.53 (t, 8H, J = 5.00 Hz), 3.59 (s, 4H), 3.74 (s, 4H), 3.86 (t, 4H, J = 5.00 Hz), 4.16 (t, 4H, J = 5.00 Hz), 6.83 (dd, 2H, J_1 = 7.50 Hz, J_2 = 0.75 Hz), 6.99 (dt, 2H, J_1 = 7.50 Hz, J_2 = 0.75 Hz), 7.32 (dt, 2H, J_1 = 7.50 Hz, J_2 = 2.50 Hz), 8.11 (dd, 2H, J_1 = 7.50 Hz, J_2 = 2.50 Hz) 8.35 (b, 2H); ms: m/z 504 (M^++2, 1.1), 503 (M^++1, 1.6), 502 (M^+, 0.5), 460 (22.6), 459 (13.2), 440 (6.8), 416 (24.2), 415 (23.7), 401 (16.3), 372 (65.3), 296 (25.8), 278 (61.6), 270 (11.6), 252 (46.3), 250 (13.2), 235 (28.9), 222 (11.6), 209 (43.2), 208 (48.4), 191 (33.7), 190 (32.6), 178 (21.1), 177 (25.8), 165 (base peak), 164 (80), 163 (64.7), 151 (27.9), 149 (31.1), 147 (32.6), 138 (24.7), 137 (25.8), 121 (94.7), 120 (61.6), 107 (15.3), 92 (15.3), 73 (36.8).

Anal. Cacld. for $C_{26}H_{34}N_2O_8$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.22; H, 6.73; N, 5.61.

1,18-Diaza-3,4;15,16-dibenzo-5,8,11,14-tetraoxacycloeicosane-2,17-dione (**19**).

This compound is a white solid, mp 175-177°; ir (potassium bromide): 603 (w), 756 (m), 930.6 (w), 1044.8 (m), 1112 (m), 1239.5 (m), 1306.7 (m), 1433 (m), 1481.3 (m), 1535 (s), 1602.2 (m), 1649.2 (s), 2887 (m), 2970 (m), 3035 (w), 3314.9 (m), 3382.1 (s) cm^{-1}; ^1H nmr (deuteriochloroform, 250 MHz): δ 3.72 (s, 4H), 3.74 (s, 4H), 3.86 (t, 4H, J = 4.50 Hz), 4.21 (t, 4H, J = 4.50 Hz), 6.91 (dd, 2H, J_1 = 8.00 Hz, J_2 = 0.75 Hz), 7.05 (dt, 2H, J_1 = 7.50 Hz, J_2 = 0.75 Hz), 7.37 (dt, 2H, J_1 = 7.60 Hz, J_2 = 1.75 Hz), 8.09 (dd, 2H, J_1 = 7.80 Hz, J_2 = 1.75 Hz), 8.20 (b, 2H); ms: m/z 416 (M^++2, 22.6), 415 (M^++1, 90.8), 414 (M^+, 6.9), 371 (7), 278 (34.3), 233 (12.3), 209 (12.9), 208 (18.3), 207 (9.1), 191 (12), 165 (46.7), 164 (60.4), 163 (11), 149 (10.4), 147 (18.4), 137 (14), 134 (10.2), 122 (8.5), 121 (base peak), 120 (47.2), 119 (11.5), 105 (16.9), 92 (34.7), 91 (22.2), 77 (16.1).

Anal. Calcd. for $C_{22}H_{26}N_2O_6$: C, 63,76; H, 6.32; N, 6.76. Found: C, 63.82; H, 6.29; N, 6.71.

Regeneration of Inorganic Solid.

The spent inorganic solid could be regenerated easily by putting it in the oven at 120° for 12 hours. The regenerated inorganic solid possessed almost the same reactivity as its original form.

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