Chem. Pharm. Bull. **40**(11) 2958—2961 (1992) Vol. 40, No. 11

Syntheses of Tertiary Tetraamines and Quaternary Pentaamines with Three and Four Methylene Chain Units

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Tertiary tetraamines and quaternary pentaamines composed of aminopropyl and/or aminobutyl groups were synthesized as authentic samples for the identification of naturally occurring branched polyamines. Four tertiary tetraamines were obtained by alkylating the free secondary amine group of diphthaloyl derivatives of *sym*-norspermidine or *sym*-homospermidine with *N*-(3-bromopropyl)phthalimide or *N*-(4-bromobutyl)phthalimide in the presence of KF-Celite. Five quaternary pentaamines were obtained by fusing triphthaloyl derivatives of the tertiary tetraamines with an excess amount of *N*-(3-iodopropyl)phthalimide or *N*-(4-iodobutyl)phthalimide. The present methods are simple and achieved high yields. The ^{13}C-NMR spectra of these branched polyamines were recorded in D_2O as fully protonated forms, and all ^{13}C chemical shifts were assigned consistently.

Keywords polyamine; tertiary tetraamine; quaternary pentaamine; alkylation; *N*-(3-bromopropyl)phthalimide; *N*-(4-bromobutyl)phthalimide; *N*-(3-iodopropyl)phthalimide; *N*-(4-iodobutyl)phthalimide; KF-Celite; ^{13}C-NMR spectrum

The polyamines such as putrescine, spermidine, and spermine are widely distributed in living organisms and play important roles in cellular processes.[1] In the last decade, many unusual aliphatic polyamines, tetraamines,[2] pentaamines,[3] and hexaamines[4] which are linear molecules containing 3 or 4 methylene chain units, were found in various bacteria, plants and other organisms. In addition, Oshima *et al.* discovered new types of polyamine, a tertiary tetraamine, tris(3-aminopropyl)amine,[5] and a quaternary pentaamine, tetrakis(3-aminopropyl)ammonium,[6] in the extreme thermophile *Thermus thermophilus*. Recently, the authors and co-workers have found new branched polyamines, a tertiary tetraamine, N^4-aminopropylspermidine, and a quaternary pentaamine, N^4-bis(aminopropyl)-spermidine, in various thermophilic eubacteria belonging to *Thermus*.[7] These findings suggest the existence of other branched polyamines as natural products. The present paper deals with systematic and high yield syntheses of a series of branched polyamines composed of aminopropyl and aminobutyl groups.

Results and Discussion

Chemical structures of four tertiary tetraamines and five quaternary pentaamines with 3 or 4 methylene chain units are listed in Table I. For the syntheses of tertiary tetraamines, corresponding secondary amines were alkylated with *N*-(3-bromopropyl)phthalimide or *N*-(4-bromobutyl)phthalimide under reflux using KF-Celite,[8] and for the syntheses of quaternary pentaamines, the corresponding tertiary amines were alkylated with *N*-(3-iodopropyl)phthalimide or *N*-(4-iodobutyl)phthalimide under a fusion condition (Chart 1).

Syntheses of Tertiary Tetraamines For the synthesis of this type of tertiary tetraamine, only methods for tris(3-aminopropyl)amine have so far been reported, *i.e.*, the alkylation of ammonia with acrylonitrile followed by reduction of the nitrile,[6,9] or the reduction of 3,3′,3″-nitrilotris(propionamide).[6] The present method is suitable for the preparation of tertiary tetraamines containing various combinations of different aminoalkyl groups.

Protected starting triamines for syntheses of a series of tertiary tetraamines were *N*,*N*-bis(3-phthalimidopropyl)-amine (**10**), which was prepared by refluxing commercially available *sym*-norspermidine and phthalic anhydride in acetic acid under conditions for the preparation of a phthaloyl derivative of a primary amine,[10] and *N*,*N*-bis(4-phthalimidobutyl)amine (**11**), which was obtained by reductive elimination of the benzyl group of *N*,*N*-bis(4-phthalimidobutyl)benzylamine prepared by alkylation of benzylamine with *N*-(4-bromobutyl)phthalimide.[8] Compound **10** or **11** was then alkylated with either *N*-(3-bromopropyl)phthalimide or *N*-(4-bromobutyl)phthalimide in the presence of KF-Celite, and the resulting triphthaloyl derivatives of tertiary tetraamines (**12**), except for **12c**, were directly precipitated from the warm filtrate after removal of KF-Celite. Compound **12c** was purified by silica gel column chromatography, but was obtained as a viscous oil. Deprotection of **12** was carried out in a usual manner using hydrazine, and the liberated tetraamines were subjected to cation exchange column chromatography to obtain their tetrahydrochloride salts (**1**—**4**). Their yields from **10** or **11** were more than 80%.

Syntheses of Quaternary Pentaamines Starting compounds for syntheses of a series of quaternary pentaamines were the triphthaloyl derivatives (**12**), which were alkylated with an excess amount (3 eq mol) of *N*-(3-iodopropyl)-

TABLE I. Synthetic Polyamines

Compd. No.	Tertiary tetraamine	Compd. No.	Quaternary pentaamine
1	$[H_2N(CH_2)_3]_3N \cdot 4HCl$	**5**	$[H_2N(CH_2)_3]_4N^+Cl^- \cdot 4HCl$
2	$[H_2N(CH_2)_3]_2N(CH_2)_4NH_2 \cdot 4HCl$	**6**	$[H_2N(CH_2)_3]_3N^+(CH_2)_4NH_2Cl^- \cdot 4HCl$
3	$H_2N(CH_2)_3N[(CH_2)_4NH_2]_2 \cdot 4HCl$	**7**	$[H_2N(CH_2)_3]_2N^+[(CH_2)_4NH_2]_2Cl^- \cdot 4HCl$
4	$[H_2N(CH_2)_4]_3N \cdot 4HCl$	**8**	$H_2N(CH_2)_3N^+[(CH_2)_4NH_2]_3Cl^- \cdot 4HCl$
		9	$[H_2N(CH_2)_4]_4N^+Cl^- \cdot 4HCl$

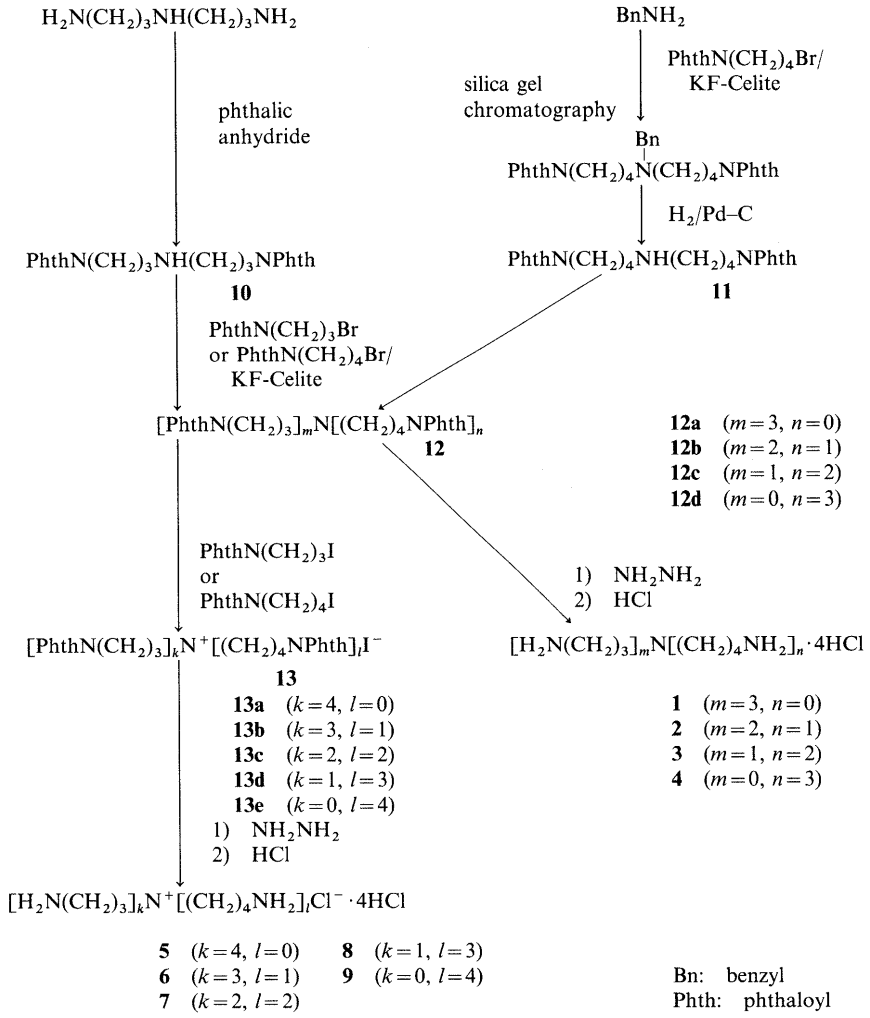

Chart 1. Syntheses of Tertiary Tetraamines and Quaternary Pentaamines

TABLE II. Yields of Tetrakis(phthalimidoalkyl)ammonium Iodide (**13**) from Tris(phthalimidoalkyl)amine (**12**) and *N*-(3-Iodopropyl)phthalimide (A) or *N*-(4-Iodobutyl)phthalimide (B)

Tertiary amine (**12**)	Reactant	Product (**13**)	Yield (%)
12a	A	**13a**	76
12a	B	**13b**	61
12b	A	**13b**	85
12b	B	**13c**	69
12c	A	**13c**	88
12c	B	**13d**	93
12d	A	**13d**	100
12d	B	**13e**	100

phthalimide or *N*-(4-iodobutyl)phthalimide under conditions of fusion at 100 °C. The *N*-iodoalkylphthalimide worked not only as a reactant but also as a suitable solvent. This fusion method is simple and provides an excellent yield as compared with the method for preparing **13a** using dioxane as a solvent reported by Oshima *et al.*[6] The yields of corresponding **13** obtained from all combinations of **12** and *N*-iodoalkylphthalimide are summarized in Table II.

As is shown in Table II, compounds **13b**, **13c** and **13d** were prepared by using two different combinations, *i.g.* **12a** and *N*-(4-iodobutyl)phthalimide, and **12b** and *N*-(3-iodopropyl)phthalimide for **13b**. There was a significant difference in yields between the two combinations, and a higher yield was observed with the use of *N*-(3-iodopropyl)phthalimide in comparison with *N*-(4-iodobutyl)phthalimide, or otherwise with the use of a tertiary tetraamine with more phthalimidobutyl groups than phthalimidopropyl groups. In addition the yields of quaternary pentaamines increased in the order of **13a**, **13b**, **13c**, **13d** and **13e**. These results indicate that increasing nucleophilicity of tertiary amine makes further alkylation easier to give the quaternary amine. Phthaloyl groups of **13** were removed with hydrazine, and the liberated quaternary pentaamines were similarly purified by cation exchange column chromatography as described for **12**, giving the quaternary pentaamines as monochloride and tetrahydrochloride salts (**5**—**9**) in yields of approximately 90% from **13**. Compounds **5** and **9** were obtained as white solids and recrystallized from MeOH–EtOH, although **5** was hygroscopic. Elemental analysis, however, suggested that an additional 1/2HCl should be added to the molecular formulas for compounds **5** and **9**. Their chemical structures should be confirmed by X-ray diffraction analysis. Compounds **6**, **7** and **8** could not be crystallized. Accordingly, their salt forms were changed to perchlorate. In these perchlorate salts, elemental analysis data supported the forms of perchlorate and tetrahydroperchlorate for the

Table III. ^{13}C-NMR Chemical Shifts of Synthetic Polyamines

Compd. No.	$(^{+}H_3N$–C_1–C_2–$C_3)_m$–N–$(C_4$–C_5–C_6–C_7–$NH_3^{+})_n$						
	C_1	C_2	C_3	C_4	C_5	C_6	C_7
1 ($m=3$, $n=0$)	37.30	22.48	50.94				
2 ($m=2$, $n=1$)	37.33	22.48	50.83	53.32	21.37	24.70	39.64
3 ($m=1$, $n=2$)	37.37	22.49	50.70	53.21	21.41	24.73	39.64
4 ($m=0$, $n=3$)				53.10	21.42	24.76	39.65
5 ($m=4$, $n=0$)	37.02	20.90	57.28				
6 ($m=3$, $n=1$)	37.10	20.89	57.04	59.73	19.82	24.47	39.64
7 ($m=2$, $n=2$)	37.15	20.90	56.78	59.49	19.79	24.50	39.64
8 ($m=1$, $n=3$)	37.19	20.82	56.50	59.23	19.75	24.54	39.65
9 ($m=0$, $n=4$)				58.98	19.74	24.59	39.67

five quaternary pentaamines.

^{13}C-NMR Data for the Tertiary Tetraamines and Quaternary Pentaamines ^{13}C-NMR spectra for the tertiary tetraamines and quaternary pentaamines were recorded in D_2O as fully protonated forms. A complete assignment of their spectra could be made by a comparative analysis of their ^{13}C chemical shifts and intensities, referring to our previous data for linear pentaamines.[8] The results are summarized in Table III, in which each carbon atom of the aminopropyl and aminobutyl groups is numbered as shown. Chemical shifts for C_1, C_2, C_5, C_6 or C_7 varied within 0.17 ppm either among tertiary tetraamines (**1**—**4**) or among quaternary pentaamines (**5**—**9**). Chemical shifts for C_3 or C_4 showed significantly lower-field values, and the values for C_3 were smaller than those for C_4 in both tertiary tetraamines and quaternary pentaamines. In addition, chemical shifts for C_3 increased in accordance with increasing numbers of aminopropyl groups in both tertiary tetraamines and quaternary pentaamines, and a similar tendency was also observed for C_4.

Experimental

^{1}H- and ^{13}C-NMR spectra were measured with a JEOL GX-270 (270 MHz) spectrometer. Chemical shifts were measured using tetramethylsilane or sodium trimethylsilyl propionate for ^{1}H-NMR, and dioxane (67.40 ppm) for ^{13}C-NMR as internal standards. High-resolution FAB-MS spectra were measured with a JMS-SX102. Melting points are uncorrected. All organic solvents and reagents used were of analytical grade.

***N,N,N*-Tris(3-aminopropyl)amine Tetrahydrochloride (1)** A solution of *sym*-norspermidine (4.04 g, 30.8 mmol) and phthalic anhydride (9.14 g, 61.7 mmol) in 30 ml of AcOH was refluxed for 1 h with stirring and evaporated *in vacuo*. The residue was extracted with $CHCl_3$ (200 ml × 2) and 4 N NH_3 (200 ml), and the combined $CHCl_3$ extract was filtered through a filter paper, and evaporated. *N,N*-Bis(3-phthalimidopropyl)amine (**10**) was recrystallized from EtOH. Yield: 78% (9.33 g, 23.9 mmol).

A solution of **10** (5.87 g, 15.0 mmol) and *N*-(3-bromopropyl)phthalimide (5.23 g, 19.5 mmol) in 75 ml of CH_3CN was refluxed in the presence of KF-Celite (15 g) under stirring for 16 h. The warm suspension was then filtered to remove KF-Celite and the filtrate was evaporated to about half the initial volume. The concentrated solution was then cooled, and practically pure *N,N,N*-tris(3-phthalimidopropyl)amine (**12a**) crystallized out. The yield of **12a** thus obtained after two crystallizations from CH_3CN was 91% (7.90 g, 13.7 mmol).

A solution of **12a** (1.0 g, 1.73 mmol) in 20 ml of EtOH containing 0.75 ml of $NH_2NH_2 \cdot H_2O$ (15.6 mmol) was refluxed for 2 h, and evaporated *in vacuo*. The residue was treated with 20 ml of 2 N HCl and the resulting phthalhydrazine was removed by filtration. The filtrate was concentrated and applied to a column of Dowex 50W-X4 (H^+ form, 25 ml). The column was washed with 2 N HCl and **1** was eluted with 3 N HCl. The fractions containing **1** were evaporated to dryness with an oil pump, and practically pure **1** was obtained as a white solid (0.55 g, 1.65 mmol, 95%). The solid was recrystallized from EtOH, mp 230—231 °C. ^{1}H-NMR (D_2O): 3.38 (6H, t), 3.13 (6H, t), 2.24—2.12 (6H, m). *Anal.* Calcd for $C_9H_{28}Cl_4N_4$: C, 32.35; H, 8.45; N, 16.77. Found: C, 32.10; H, 8.15; N, 16.73.

***N,N*-Bis(3-aminopropyl)-*N*-(4-aminobutyl)amine Tetrahydrochloride (2)** This compound was prepared in the same manner as described for **1**, except for the use of *N*-(4-bromobutyl)phthalimide at the alkylation of **10**. The resulting *N,N*-bis(3-phthalimidopropyl)-*N*-(4-phthalimidobutyl)-amine (**12b**) was obtained as white crystals (93%). Compound **2** was then prepared from **12b** (0.70 g, 1.18 mmol) and obtained as an oil (0.37 g, 1.07 mmol, 91%), which was crystallized from EtOH. mp 176—178 °C. ^{1}H-NMR (D_2O): 3.38—3.28 (6H, m), 3.14—3.07 (6H, m), 2.19—2.10 (4H, m), 1.9—1.7 (4H, m). *Anal.* Calcd for $C_{10}H_{30}Cl_4N_4$: C, 34.50; H, 8.68; N, 16.09. Found: C, 34.54; H, 8.42; N, 16.02.

***N,N*-Bis(4-aminobutyl)-*N*-(3-aminopropyl)amine Tetrahydrochloride (3)** *N,N*-Bis(4-phthalimidobutyl)benzylamine (5.40 g, 10.6 mmol), which was prepared from benzylamine and 2 eq of *N*-(4-bromobutyl)phthalimide according to the reported method,[8] was subjected to reductive elimination of the benzyl group in 30 ml of AcOH at 70 °C for 20 h under an H_2 atmosphere in the presence of 10% Pd–C (300 mg). The catalyst was then filtered off and the filtrate was evaporated *in vacuo*. The residue was shaken with 100 ml of $CHCl_3$ and 100 ml of 4 N NH_3, and the $CHCl_3$ extract was filtered through a filter paper and evaporated to dryness. *N,N*-Bis(4-phthalimidobutyl)amine (**11**) was recrystallized from EtOH. Yield: 81% (3.59 g, 8.57 mmol).

The alkylation of **11** (2.00 g, 4.77 mmol) with *N*-(3-bromopropyl)phthalimide (1.66 g, 6.20 mmol) in 20 ml of CH_3CN and KF-Celite (5 g) was similar to that described for **12a**. After the removal of KF-Celite and CH_3CN, the residue was chromatographed on a silica gel (50 g) column with benzene–acetone (5 : 1). Practically pure *N,N*-bis(4-phthalimidobutyl)-*N*-(3-phthalimidopropyl)amine (**12c**) was obtained as a viscous pale yellow oil (2.76 g, 4.55 mmol, 95%). Compound **3** was then prepared from **12c** (1.0 g, 1.65 mmol) in the same manner as described for **1**. Oily **3** thus obtained (0.59 g, 1.63 mmol, 99%) was crystallized from EtOH. mp 186—188 °C. ^{1}H-NMR (D_2O): 3.34—3.25 (6H, m), 3.14—3.03 (6H, m), 2.21—2.09 (2H, m), 1.9—1.7 (8H, m). *Anal.* Calcd for $C_{11}H_{32}Cl_4N_4$: C, 36.48; H, 8.90; N, 15.47. Found: C, 36.20; H, 8.67; N, 15.21.

***N,N,N*-Tris(4-aminobutyl)amine Tetrahydrochloride (4)** This compound was prepared in the same manner as described for **3**, except for the use of *N*-(4-bromobutyl)phthalimide at the alkylation of **11**. The resulting *N,N,N*-tris(4-phthalimidobutyl)amine (**12d**) was obtained as white crystals (86%). Compound **4** was then prepared from **12d** (0.70 g, 1.13 mmol) in the same manner as described for **1**. The white solid thus obtained (0.39 g, 1.04 mmol, 92%) was recrystallized from EtOH. mp 286—288 °C. ^{1}H-NMR (D_2O): 3.25 (6H, t), 3.05 (6H, t), 1.9—1.7 (12H, m). *Anal.* Calcd for $C_{12}H_{34}N_4Cl_4$: C, 38.31; H, 9.11; N, 14.89. Found: C, 38.02; H, 8.85; N, 14.80.

Tetrakis(3-aminopropyl)ammonium Chloride Tetrahydrochloride (5) Tetrakis(3-phthalimidopropyl)ammonium iodide (**13a**) was synthesized as follows: **12a** (1.00 g, 1.73 mmol) and *N*-(3-iodopropyl)phthalimide (1.63 g, 5.19 mmol), which was prepared by reacting *N*-(3-bromopropyl)phthalimide with NaI,[6] were placed in the bottom of a light-shielded small flask (20 ml) with a stirring bar and heated at 100 °C under an Ar atmosphere. The melted mixture was stirred, and it solidified within 1 h. After heating for 3 h, the solid was finely crushed with a spatula and washed well with hot benzene on a glass filter. The remaining solid was practically pure **13a** as a pale yellow solid (1.18 g, 1.32 mmol, 76%).

Deprotection of phthaloyl groups of **13a** (500 mg, 0.560 mmol) with $NH_2NH_2 \cdot H_2O$ (0.32 ml) and application to a column of Dowex 50W-X4 (10 ml) were carried out in the same manner as described for **1**, except for the use of 4 N HCl as the solvent for eluting **5** from the column. After a complete drying of fractions containing **5** with an oil pump, a pale yellow solid was obtained (230 mg, 0.538 mmol, 96%). This solid was hygroscopic and was recrystallized from MeOH–EtOH to give white crystals. mp 163—165 °C. ^{1}H-NMR (D_2O): 3.57 (8H, t), 3.14 (8H, t), 2.28—2.15 (8H, m). Exact FAB-MS *m/z*: Calcd for $C_{12}H_{32}N_5$: 246.2658. Found: 246.2647. The result of elemental analysis suggested **5**·1/2HCl. *Anal.* Calcd for $C_{12}H_{36.5}Cl_{5.5}N_5$: C, 32.32; H, 8.25; N, 15.70. Found: C, 32.18; H, 8.32; N, 15.40.

The salt form of **5** was changed using perchloric acid and the perchlorate and tetrahydroperchlorate salt was obtained as white crystals. mp > 300 °C. *Anal.* Calcd for $C_{12}H_{36}Cl_5N_5O_{20}$: C, 19.28; H, 4.85; N, 9.37. Found: C, 18.96; H, 4.79; N, 9.02.

Tris(3-aminopropyl)-(4-aminobutyl)ammonium Chloride Tetrahydrochloride (6) Tris(3-phthalimidopropyl)-(4-phthalimidobutyl)ammonium iodide (**13b**) was prepared with two different combinations of reagents, *i.e.*, **12b** (700 mg, 1.18 mmol) and *N*-(3-iodopropyl)phthalimide (1.12 g, 3.56 mmol), and **12a** (1.00 g, 1.73 mmol) and *N*-(4-iodobutyl)phthalimide

(1.71 g, 5.19 mmol) which was similarly prepared according to the literature.[6] The reaction conditions were almost the same as those described for **13a**. The yields of **13b** were 85% and 61%, respectively (Table II). Deprotection of phthaloyl groups of **13b** (500 mg, 0.551 mmol) followed by column chromatography gave **6** as a pale yellow oil (235 mg, 0.532 mmol, 97%). ^{1}H-NMR (D_2O): 3.56—3.47 (8H, m), 3.17—3.07 (8H, m), 2.26—2.15 (6H, m), 1.95—1.7 (4H, m). Exact FAB-MS *m/z*: Calcd for $C_{13}H_{34}N_5$: 260.2814. Found: 260.2830.

The perchlorate and tetrahydroperchlorate salt was obtained from **6** as crystals. mp 156—158 °C. *Anal.* Calcd for $C_{13}H_{38}Cl_5N_5O_{20}$: C, 20.50; H, 5.03; N, 9.19. Found: C, 20.15; H, 4.97; N, 8.97.

Bis(4-aminobutyl)-bis(3-aminopropyl)ammonium Chloride Tetrahydrochloride (7) Bis(4-phthalimidobutyl)-bis(3-phthalimidopropyl)ammonium iodide (**13c**) was also prepared with two different combinations of reagents, *i.e.*, **12c** (0.60 g, 0.99 mmol) and *N*-(3-iodopropyl)phthalimide (0.94 g, 3.0 mmol), and **12b** (700 mg, 1.18 mmol) and *N*-(4-iodobutyl)-phthalimide (1.17 g, 3.56 mmol). The yields of **13c** were 88% and 69%, respectively (Table II). Compound **7** was similarly prepared from **13c** (511 mg, 0.555 mmol) and obtained as a pale yellow oil (233 mg, 0.512 mmol, 92%). ^{1}H-NMR (D_2O): 3.51—3.42 (8H, m), 3.15—3.06 (8H, m), 2.25—2.15 (4H, m), 1.95—1.7 (8H, m). Exact FAB-MS *m/z*: Calcd for $C_{14}H_{36}N_5$: 274.2971. Found: 274.2988.

The perchlorate and tetrahydroperchlorate salt was obtained from **7** as crystals. mp 241—242 °C. *Anal.* Calcd for $C_{14}H_{40}Cl_5N_5O_{20}$: C, 21.68; H, 5.20; N, 9.03. Found: C, 21.61; H, 5.01; N, 9.01.

Tris(4-aminobutyl)-(3-aminopropyl)ammonium Chloride Tetrahydrochloride (8) Tris(4-phthalimidobutyl)-(3-phthalimidopropyl)ammonium iodide (**13d**) was also prepared with two different combinations of reagents, *i.e.*, **12d** (700 mg, 1.13 mmol) and *N*-(3-iodopropyl)phthalimide (1.07 g, 3.39 mmol), and **12c** (600 mg, 0.990 mmol) and *N*-(4-iodobutyl)phthalimide (977 mg, 2.97 mmol). The yields of **13d** were almost 100% and 93%, respectively (Table II). Compound **8** was similarly prepared from **13d** (500 mg, 0.535 mmol) and obtained as a pale yellow oil (222 mg, 0.473 mmol, 88%). ^{1}H-NMR (D_2O); 3.47—3.38 (8H, m), 3.14—3.06 (8H, m), 2.25—2.10 (2H, m), 1.9—1.7 (12H, m). Exact FAB-MS *m/z*: Calcd for $C_{15}H_{38}N_5$: 288.3127. Found: 288.3139.

The perchlorate and tetrahydroperchlorate salt was obtained from **8** as crystals. mp 286—287 °C. *Anal.* Calcd for $C_{15}H_{42}Cl_5N_5O_{20}$: C, 22.81; H, 5.36; N, 8.87. Found: C, 22.71; H, 5.08; N, 8.69.

Tetrakis(4-aminobutyl)ammonium Chloride Tetrahydrochloride (9) Tetrakis(4-phthalimidobutyl)ammonium iodide (**13e**) was prepared with **12d** (700 mg, 1.13 mmol) and *N*-(4-iodobutyl)phthalimide (1.12 g, 3.39 mmol) and obtained quantitatively. Compound **9** was similarly prepared from **13e** (500 mg, 0.527 mmol) and obtained as a white solid (230 mg, 0.476 mmol, 90%), which was recrystallized from MeOH–EtOH. mp 269—271 °C. ^{1}H-NMR (D_2O): 3.37 (8H, t), 3.08 (8H, t), 1.9—1.7 (16H, m). Exact FAB-MS *m/z*: Calcd for $C_{16}H_{40}N_5$: 302.3284. Found: 302.3281. The result of elemental analysis suggested $9 \cdot 1/2HCl$. *Anal.* Calcd for $C_{16}H_{44.5}Cl_{5.5}N_5$: C, 38.28; H, 8.93; N, 13.95. Found: C, 38.59; H, 8.77; N, 13.87.

The perchlorate and tetrahydroperchlorate salt was obtained from **9** as crystals. mp >300 °C. *Anal.* Calcd for $C_{16}H_{44}Cl_5N_5O_{20}$: C, 23.91; H, 5.52; N, 8.71. Found: C, 23.89; H, 5.34; N, 8.43.

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