CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis

p-tert-Butylcalix[4]arene was prepared by the condensation of *p-tert*-butylphenol with formaldehyde in a minimum amount of sodium hydroxide and diphenylether was used as solvent, as described by Gutsche [42]. The recommended conditions for refluxing were necessary to yield the desired tetrameric unit. The yield of *p-tert*-butylcalix[4]arene prepared by this method (2.1.1) was 60% after recrystallization in toluene. This compound was checked by ^{1}H-NMR ($CDCl_3$) spectroscopy and the spectrum is shown in Figure A.1. ArO**H** was observed as a singlet, at 10.32 ppm and HOAr**H** a singlet, at 7.17 ppm. Ar$C\mathbf{H}_A\mathbf{H}_B$Ar appeared as an AB system at 4.20 and 3.44 ppm with a coupling constant of 13.0 Hz. The *tert*-butyl groups were observed as a singlet at 1.99 ppm. The ^{1}H-NMR data shows that the synthesized *p-tert*-butylcalix[4] arene was in cone conformation. The mass spectrum (EI^+), Figure A.20, reveals the molecular peak at 648 (100%). The elemental analysis showed that the *p-tert*-butylcalix[4]arene contained one toluene molecule.

2[(1-Formyl-2-phenyl)oxy]ethylbromide (2a) was prepared according to a reported procedure[43]. Salicylaldehyde was reacted with an excessive amount of 1,2-dibromoethane while refluxing in acetonitrile under nitrogen atmosphere. The reaction yielded 2[(1-formyl-2-phenyl)oxy]ethylbromide (2a) as a major product (51%) and 2,2'-(1,2-dioxyethane)*bis*benzaldehyde (2b) as a

minor product (2%). The characteristic of (2a) is a white solid, Mp. 58°C. ^{1}H-NMR ($CDCl_3$) spectrum is shown in Figure A.2 and ^{1}H-NMR analysis is shown in Table 3.2. The spectrum confirms the proposed structure for (2a), Scheme I.

The minor product (2b) is a disubstituted product which can be confirmed by its ^{1}H-NMR spectrum in deutereted chloroform (Figure A3 and Table 3.3).

25,27-*bis*[2-[(1-formyl-2-phenyl)oxy]ethyl]-*p-tert*-butylcalix[4]arene (3) was prepared from a reaction between 2[(1-formyl-2-phenyl)oxy] ethylbromide (2a) and *p-tert*-butylcalix[4]arene by refluxing the reaction mixture in acetonitrile under nitrogen atmosphere (Scheme I). The reaction was a replacement of hydroxyl protons by alkyl groups with a loss of HBr with an aid of potassium carbonate base. The reaction was complete in 63 hours. The pure 1,3-dialdehyde derivative (3) was obtained after a chromatographic separation on a silica gel column with dichloromethane as eluent with 67% yield. The ^{1}H-NMR ($CDCl_3$) spectrum of (3) is displayed in Figure A.4. The analysis of the spectrum (Table 3.4) showed that (3) existed as 1,3-disubstituted cone conformation, ArCH_AH_BAr appeared as an AB system at 4.28 and 3.28 ppm with a coupling constant of 13.0 Hz, while HOAr-*t*-C_4H_9 and ROAr-*t*-C_4H_9 appeared at 1.26 and 1.03 ppm, respectively.

Scheme II presents synthetic pathways for constructing Schiff base derivatives of *p-tert*-butylcalix[4]arene, 4(a-e) by condensing the dialdehyde derivative (3) with appropriate primary diamines; 1,3-propylenediamine, 1,4-butylenediamine, diethylene triamine, triethylene tetramine, and tetraethylene pentamine. The dialdehyde derivative (3) was refluxed with excessive amount (10%) of the appropriate primary diamino compound in

acetonitrile-methanol for 9 hours. The reaction mixture precipitated as a white solid for 4(a-c) and a yellow solid for 4(d-e). The yields were 86%, 88%, 97%, 24% and 28%, respectively. The reaction of (3) and diethylenetriamine proceeded with a faster rate and higher yield than the rest, this could be due to a, more or less, better fit of the primary diamine bridge onto the calixarene unit, thus leading to a more effective ring closure. All the products were white powders except for (4d) and (4e) which were pale yellow. They were all solids melting with decomposition at temperatures ranging from 192°C to 300°C. They were characterized by ^{1}H-NMR, FAB$^+$ MS techniques and elemental analysis. From the ^{1}H-NMR spectra, 4(a-b) were deduced to be 1,3-bridge-*p*-*tert*-butylcalix[4]arene derivatives in cone conformation due to the presence of only two singlets for the *tert*-butyl groups at 1.30 and 0.87 ppm for (4a), 1.29 and 0.83 ppm for (4b), one AB system for Ar**C**$\mathbf{H_2}$Ar at 4.44 and 3.27 ppm (J = 13.0 Hz) for (4a) and 4.44 and 3.22 ppm (J = 13.0 Hz) for (4b) [38].

The imine protons appeared at 8.73 ppm for (4a) and 8.81 ppm for (4b). When the bridge was extended to contain more than 4 carbon atoms, the ^{1}H-NMR spectra of the obtained Schiff base derivatives, 4(c-e), are more complicated. However, all three compounds exhibited **H**C=N signal in the same region as those of (4a) and (4b). (4c) gave two **H**C=N signals at 8.77 and 8.67 ppm, indicating two conformations in the product. The integration ratios of signals in Figure A.7 were consistent with the structure proposed for (4c) in Scheme II. The other conformation could be partial cone which was not attempted to be assigned in this study. The elemental analysis and mass spectral data are consistent with the molecular formula of (4c). The ^{1}H-NMR spectra of (4d) and (4e), Figures A.8 and A.9 , were obtained with difficulty due to the low solubility of the Schiff base in deuterated chloroform. The imine protons appeared at 8.73 and 8.72 ppm, respectively. The complex pattern for *tert*-$C_4\mathbf{H}_9$

indicates a mixture of conformations with the same empirical formulas. The elemental analysis data of both (4d) and (4e) compounds were consistent with the proposed empirical formulas with one methanol molecule in the structure.

4(c-e) are novel compounds, constructed as models for calix[4]arene containing more than two nitrogen atoms in the bridging cap. The yellow color and low solubility (4d) and (4e) could indicate the existence of polymeric substance resulting from the connection of the long aza-chain with two calix[4] arene units.

The acidic form of the Schiff base derivatives could be synthesized by hydrogenating the corresponding Schiff base compounds with $NaBH_4$ in tetrahydrofuran and acidifying the product of the reduction reaction with HCl in methanolic solution as reported elsewhere [43]. 5(a-c) were obtained in good yields, 95%, 81%, and 89%, respectively. $N\mathbf{H}_2^+$ signals appeared in the down field region, 9.80 ppm for (5a) and 9.13 ppm for (5b). 5(c) exhibited two $N\mathbf{H}_2^+$ signals at 9.99 and 9.56 ppm, with integation of 1 : 2. $ArC\mathbf{H}_2NH_2^+$ appeared at 4.63, 4.60 and 4.69 ppm, respectively, due to the influence of the positive charge on the nitrogen atom. Interestingly, (5c) was obtained in pure cone conformation, despite the presence of other conformation in its precursor (4c). Mass spectrum, Figure A.22, shows a peak at 1016.4 which indicates a loss of HCl molecules from the original structure in the spectrometer. The same effect was observed for a mass spectral analysis of (5a) and (5b) [45]. (5c) serves as a model with three ammonium sites for anion complexation study.

^{1}H-NMR spectra of (5d) and (5e), Figures A.13 and A.14, are not well defined. However, the $N\mathbf{H}_2^+$ signals can be observed at 9.15 and 9.25ppm, respectively.The synthesized (5d) and (5e) are believed to be acidic forms of (4d) and (4e).

Basic forms of 5(a-c) could be obtained by neutralizing the corresponding acidic form 5(a-c) with sodium hydroxide as shown in Scheme IV. 6(a-c) were obtained in good yields, 80%, 49% and 89%, respectively. The NH_2^+ signals in the acidic forms disappeared from the ^{1}H-NMR spectra of 6(a-c). ArCH_2N signals shifted noticeably to upfield region, from 4.63 (5a) to 3.83 ppm (6a), 4.60 (5b) to 3.82 ppm (6b) and 4.69 (5c) to 3.82 ppm (6c). Methylene protons in the bridging cap also moved in the same fashion. Mass spectrum of (6c), Figure A.23, and elemental analysis confirmed the proposed structure for (6c).

Two reactants, (6a) and (6c) were selected in the preparation of methylammonium derivatives of calix[4]arene for anion complexation study (Scheme V).

The difference in number of nitrogen atoms in the bridge may provide a conclusion about anion complexing ability of the synthesized molecules. (7a) and (7b) were obtained by methylating (6a) and (6c), respectively, first with methyl iodide and then with dimethylsulfate. OCH_3 signals appear at 3.51 ppm for (7a) and 3.59 ppm for (7b). $N^+(CH_3)_2$ signals appear at 3.22 ppm for (7a) while (7b) gave two signals at 3.59 ppm, $CH_2N^+(CH_3)_2CH_2$ and 3.29 ppm, $ArCH_2N^+(CH_3)_2$. ArCH_2N signals shifted noticeably to upfield region, from 3.83 (6a) to 4.84 ppm (7a) and 3.82 (6c) to 4.88 ppm (7b).

(7b) was synthesized in the same fashion as (7a) with 54% yield. Its ^{1}H-NMR spectrum (Figure A.19) is consistent with the proposed structure in Scheme V. $CH_2N^+(CH_3)_2CH_2$ appeared at higher chemical Schiff (3.59 ppm) than $ArCH_2N^+(CH_3)_2$ (3.29 ppm) as was the case for $CH_2NH_2^+CH_2$ (9.99 ppm) and $ArCH_2NH_2^+$ (9.56 ppm) in (5c). (7b) is believed to exist with HSO_4^- as

counter anions as in (7a) [44]. Mass spectrum of (7b), Figure A.19 shows a peak at 1086.7, corresponding to its basic form *i.e.* a loss of three methyl groups from the diammonium derivative [44]. This observation is consistent with those observed in the mass spectra of (5a), (5c) and (7a), that is the second protons or methyl groups on the nitrogen atoms would be clipped off in the ionization chamber.

The anion complexation study of (5a) has been studied in detail by Thammapatanajit [46]. The novel compounds (5c) and (7b), synthesized in this work, were brought to their anion complexing study along with (7a). The chosen compounds were of different number of nitrogen atoms (2N and 3N) and different ammonium salt types NH_2^+ and $N(CH_3)_2^+$, on the bridge of *p-tert*-butylcalix[4]arenes of interest.

3.2 Complexation Study

Ligand (5c) reacted heterogeneously with sodium nitrate in dichloromethane for 36 hours. In some reactions, the unreacted sodium nitrate was observed and filtered off. The ^{1}H-NMR spectra of the residue after filtration (Figures A. 27-35, Table 3.2.1) show up field shifts for $\mathbf{CH_2}$-NH_2^+-$\mathbf{CH_2}$ and Ar-CH_2-NH_2^+-$\mathbf{CH_2}$ signals. Typical mole ratio plots are presented in Figures A.25 and A.26, respectively, suggesting a 1:1 inclusion complex. These upfield shifts indicated an incorporation of highly negative group onto ligand (5c), *i.e.* a replacement of Cl^- by NO_3^- [46]. The magnitude of the displacement of $\mathbf{CH_2}$-NH_2^+-$\mathbf{CH_2}$ signal was considerably large, 40.9 Hz, as compared with 20.0 Hz of Ar-CH_2-NH_2^+-$\mathbf{CH_2}$ signal displacement observed in the interaction between (5a) and nitrate by Thammapatanagit and co-worker [46]. This could imply a stronger interaction in the triammonium derivative (5c) than the diammonium derivative (5a) which was also observed by Motetaitis [47].

Interestingly, Ar-$\mathbf{CH_2}$-NH_2^+ signal was not significantly disturbed by the nitrate inclusion, indicating that the nitrate ion probably resided within the ammonium bridge, thus was too remote to significantly affect the Ar-$\mathbf{CH_2}$-NH_2^+ protons.

The interaction between ligand (5c) and sodium carbonate was similar to that observed with sodium nitrate. Typical mole ratio plots Figures A.36 and A.37 for $\mathbf{CH_2}$-NH_2^+-$\mathbf{CH_2}$ and Ar-CH_2-NH_2^+-$\mathbf{CH_2}$ signals, respectively, also suggest a 1:1 type for carbonate complex.

The interaction between CO_3^{2-} and (5c) is stronger than that of NO_3^-, as can be observed from the ΔHz magnitudes (studied on a 500 MHz instrument for the carbonate complex study and a 200 MHz instrument for the nitrate complex study). The stronger interaction could probably be due to a higher negative charge of CO_3^{2-} than NO_3^- and a better fit for CO_3^{2-} in the ammonium bridge than NO_3^-.

A competitive study (2.2.3.1) between nitrate and carbonate for (5c) showed the substitution of the included nitrate ion in (5c) by the carbonate ion. Figure A.47 shows a normal upfield shift for $CH_2NH_2^+CH_2$ and $ArCH_2NH_2^+CH_2$ from 3.99 and 3.69 ppm to 3.78 and 3.56 ppm, respectively, for NO_3^- : (5c) ratio of 1:1. When the same number of equivalence of CO_3^{2-} was added in this reaction mixture, both signals shifted further to be at 2.91 and 2.89 ppm, respectively (Figure A.48). These final chemical shifts are in accordance with those observed in the carbonate complexation study. When both anions were mixed with (5a) in the same reaction mixture (2.2.3.2), the same results of carbonate inclusion was observed (Figure A.49). It can be concluded that (5c) has a recognition for $CO_3^{2-} > NO_3^- > Cl^-$.

(5a) changed to its basic form when interacted with carbonate ion [46]. This is not the case for (5c) since upfield shifts were observed in all carbonate complexation studies (vide supra). This implies lower K_a values of the ammonium protons in (5c) than in (5a).

One of the objectives of this study was to synthesize methyl ammonium salt derivatives of *p-tert*-butylcalix[4]arene which would not be affected by the basicity of the studied anions. When the methyl ammonium salt (7b) reacted with nitrate ion at A : L ratios 1 : 1 and 4 : 1, the reaction

mixture turned yellow after the contact of the reactants. However, the ^{1}H-NMR spectra (Figures A.56 and A.57) are similar to that of (7b). The extent of the interaction between (7b) and nitrate ion may have been too weak to be detected by ^{1}H-NMR spectroscopic technique. A steric hindrance from the methyl groups around the bridging cap could have been a major contribution for the observed weak interaction. When the anion was changed to carbonate ion (A : L = 1 : 1), a slight upfield displacement for OCH_2CH_2O protons was observed (~0.1 ppm). This may signify a weak interaction between carbonate ion and (7b). The carbonate anion may have lied low from the positive charge of nitrogen sites, due to the steric effect mentioned above, resulting in the upfield shift of OCH_2CH_2O signals. The stronger interaction of carbonate ion than nitrate to (5c) was also observed in this study (vide supra).

The anion complexation study between (7a) and nitrate or carbonate ion revealed similar results as in the case of (7b). The reaction between (7a) and nitrate ion, A : L = 1 : 1 and 4 : 1, gave ill-defined ^{1}H-NMR spectra, Figures A.50 and A.51 , with a color change from colorless to yellow as observed in the case of (7b) and nitrate ion. No significant change in ^{1}H-NMR spectra of reaction between (7a) and carbonate ion, A : L = 1 : 1 and 4 : 1, was observed. However, the study of (5a) with nitrate ion [46] showed L_2A, LA and LA_2 were formed during the course of the study. It is concluded, at this stage, that the interaction between (7a) and nitrate or carbonate ion is too weak to be detected by NMR-spectroscopic technique. A stronger interaction of carbonate ion than nitrate ion was not observed in this case.

Table 3.1 ^{1}H-NMR analysis of (1)

Chemical Shift (ppm)	Multiplicity	Number of protons	Assignment
10.32	singlet	4H	ArO**H**
7.17	singlet	8H	HOAr**H**
4.20 , 3.44	2 doublets J = 13.3 Hz	8H	AB system ArCH_AH_BAr
1.19	singlet	36H	HOAr-*t*-C_4H_9

Table 3.2 ^{1}H-NMR analysis of (2a)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
10.47	singlet	1H	C**H**O
7.85	doublet J = 7.7 Hz	1H	H_a
7.55	triplet J = 8.2 Hz	1H	H_b
7.07	triplet J = 7.1 Hz	1H	H_c
6.96	doublet J = 8.4 Hz	1H	H_d
4.42	triplet J = 5.0 Hz	2H	OCH_2CH_2Br
3.70	triplet J = 5.0 Hz	2H	OCH_2CH_2Br

Table 3.3 ^{1}H-NMR analysis of (2b)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
10.45	singlet	2H	CHO
7.80	doublet J = 7.8 Hz	2H	H_a
7.59	triplet J = 6.1 Hz	2H	H_b
7.10	triplet J = 7.2 Hz	2H	H_c
7.07	doublet J = 8.0 Hz	2H	H_d
4.53	singlet	4H	OCH_2CH_2O

Table 3.4 ^{1}H-NMR analysis of (3)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
10.47	singlet	2H	CHO
7.81	doublet J = 7.7 Hz	2H	H_a
7.53 , 7.49	multiplet	2H	H_b
7.44	singlet	2H	ArOH
6.98 , 6.93	multiplet	4H	H_c , H_d
6.99	singlet	4H	HOArH
6.84	singlet	4H	ROArH
4.40 - 4.37	multiplet	8H	OCH_2CH_2O
4.28 , 3.28	2 doublets J = 13.0 Hz	8H	AB system $ArCH_AH_BAr$
1.23	singlet	18H	HOAr-*t*-C_4H_9
0.99	singlet	18H	ROAr-*t*-C_4H_9

Table 3.5 ^{1}H-NMR analysis of (4a)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
8.73	singlet	2H	CHN
7.83	doublet J = 7.8 Hz	2H	H_a
7.26-7.18	multiplet	2H	H_b
7.06	singlet	4H	HOAr**H**
6.80-6.62	multiplet	10H	H_c, H_d ROAr**H** and Ar**OH**
4.44 , 3.27	2 doublets J = 13.0 Hz	8H	AB system ArCH_AH_BAr
4.27	singlet(broad)	8H	OCH_2CH_2O
3.24	singlet	4H	NCH_2CH_2
1.88	multiplet	2H	$CH_2CH_2CH_2$
1.30	singlet	18H	HOAr-*t*-C_4H_9
0.87	singlet	18H	ROAr-*t*-C_4H_9

Table 3.6 ^{1}H-NMR analysis of (4b)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
8.81	singlet	2H	CHN
7.90	doublet J = 7.7 Hz	2H	H_a
7.29	triplet J = 7.7 Hz	2H	H_b
7.03	singlet	4H	HOAr**H**
6.96	multiplet	2H	H_c
6.83	doublet J = 8.2 Hz	2H	H_d
6.62	singlet	4H	ROAr**H**
6.47	singlet	2H	ArO**H**
4.44 , 3.22	2 doublets J = 13.0 Hz	8H	AB system $ArCH_AH_BAr$
4.33	singlet (broad)	8H	OCH_2CH_2O
3.15	multiplet	4H	NCH_2CH_2
1.47	multiplet	4H	$CH_2CH_2CH_2CH_2$
1.29	singlet	18H	HOAr-*t*-C_4H_9
0.83	singlet	18H	ROAr-*t*-C_4H_9

Table 3.7 ^{1}H-NMR analysis of (4c)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
8.77 , 8.67	2 singlet	2H	C**H**N
7.85-6.18	multiplet	18H	H_a , H_b , HOAr**H**
			H_c , H_d
			ROAr**H** and Ar**OH**
4.80-3.30	multiplet	16H	Ar**CH$_2$**NH
			O**CH$_2$CH$_2$**O
			N**CH$_2$CH$_2$**N
4.41-3.33	2 doublets	8H	AB system Ar**CH$_A$H$_B$**Ar
	J = 13.0 Hz		
1.50-0.70	multiplet	36H	HOAr-*t*-C$_4$**H$_9$**
			ROAr-*t*-C$_4$**H$_9$**

Table 3.8 ^{1}H-NMR analysis of (4d)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
8.73	singlet	2H	CHN
7.82-6.58	multiplet	18H	H_a , H_b, HOAr**H** , H_c , H_d ROAr**H** and Ar**OH**
4.70-3.01	multiplet	28H	AB system ArCH_AH_BAr OCH_2CH_2O NCH_2CH_2 and N**H**
1.30-0.82	multiplet	36H	HOAr-*t*-C_4H_9 ROAr-*t*-C_4H_9

Table 3.9 ^{1}H-NMR analysis of (4e)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
8.72	singlet (broad)	2H	CHN
7.94 - 6.57	multiplet	18H	H_a , H_b , HOAr**H** H_c , H_d ROAr**H** and Ar**OH**
4.76 - 1.73	multiplet	35H	AB system ArCH_AH_BAr OCH_2CH_2O, NCH_2CH_2N and N**H**
1.27-0.83	multiplet	36H	HOAr-*t*-C_4H_9 ROAr-*t*-C_4H_9

Table 3.10 ^{1}H-NMR analysis of (5a)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
9.80	singlet (broad)	4H	N**H**
7.39 - 7.29 and 6.93 - 6.83	multiplet	8H	H_a , H_b, H_c and H_d
6.98	singlet	4H	HOAr**H**
6.76	singlet	2H	Ar**OH**
6.71	singlet	4H	ROAr**H**
4.63	singlet (broad)	4H	Ar$\mathbf{CH_2}$NH
4.36 , 3.22	2 doublets J = 13.0 Hz	8H	AB system Ar$\mathbf{CH_AH_B}$Ar
4.22	singlet (broad)	8H	O$\mathbf{CH_2CH_2}$O
3.69	singlet (broad)	4H	N$\mathbf{CH_2}$$CH_2$
2.83	singlet (broad)	2H	$CH_2\mathbf{CH_2}CH_2$
1.24	singlet	18H	HOAr-*t*-$C_4\mathbf{H_9}$
0.86	singlet	18H	ROAr-*t*-$C_4\mathbf{H_9}$

Table 3.11 ^{1}H-NMR analysis of (5b)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
9.13	singlet (broad)	4H	N**H**
7.40	doublet J = 7.1 Hz	2H	H_a
7.23 - 7.17	multiplet	2H	H_b
6.97	singlet	4H	HOAr**H**
6.87 - 6.74	multiplet	4H	H_c and H_d
6.78	singlet	2H	ArO**H**
6.68	singlet	4H	ROAr**H**
4.60	singlet (broad)	4H	ArCH_2NH
4.32 , 3.15	2 doublets J = 13.0 Hz	8H	AB system ArCH_AH_BAr
4.18	singlet (broad)	8H	OCH_2CH_2O
3.18	singlet	4H	NCH_2CH_2
2.26	singlet (broad)	4H	$CH_2CH_2CH_2CH_2$
1.23	singlet	18H	HOAr-*t*-C_4H_9
0.85	singlet	18H	ROAr-*t*-C_4H_9

Table 3.12 ^{1}H-NMR analysis of (5c)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
9.99	singlet (broad)	2H	$CH_2N\mathbf{H_2}^+CH_2$
9.56	singlet (broad)	4H	$ArCH_2N\mathbf{H_2}^+$
7.43	doublet J = 6.9 Hz	2H	H_a
7.39	multiplet	2H	H_b
6.97	singlet	4H	HOAr**H**
6.84 - 6.58	multiplet	6H	H_c, H_d and ArO**H**
6.67	singlet	4H	ROAr**H**
4.69	singlet (broad)	4H	$ArC\mathbf{H_2}NH$
4.26 , 3.19	2 doublets J = 13.0 Hz	8H	AB system $ArC\mathbf{H_A}\mathbf{H_B}Ar$
4.25	singlet (broad)	8H	$OC\mathbf{H_2}C\mathbf{H_2}O$
3.99	singlet (broad)	4H	$C\mathbf{H_2}^+NH_2C\mathbf{H_2}$
3.69	singlet (broad)	4H	$ArCH_2NH_2^+C\mathbf{H_2}$
1.22	singlet	18H	HOAr-*t*-$C_4\mathbf{H_9}$
0.85	singlet	18H	ROAr-*t*-$C_4\mathbf{H_9}$

Table 3.13 ^{1}H-NMR analysis of (5d)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
9.15	singlet (broad)	8H	N**H**
7.30 - 6.71	multiplet	18H	H_a , H_b , HOAr**H**
			H_c , H_d , ArO**H**
			and ROAr**H**
4.70 - 2.84	multiplet	32H	ArCH_2NH
			AB system ArCH_AH_BAr
			OCH_2CH_2O
			and NCH_2CH_2
1.23	singlet	18H	HOAr-*t*-C_4H_9
0.87	singlet	18H	ROAr-*t*-C_4H_9

Table 3.14 ^{1}H-NMR analysis of (5e)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
9.25	singlet (broad)	10H	N**H**
7.42 - 6.40	multiplet	18H	H_a , H_b , HOAr**H**
			H_c , H_d , Ar**O**H
			and ROAr**H**
4.72 - 2.74	multiplet	36H	Ar**C**H_2NH
			AB system Ar**C**$H_A$$H_B$Ar
			O**C**H_2**C**H_2O
			and N**C**H_2**C**H_2
1.19	singlet	18H	HOAr-*t*-C_4H_9
0.89	singlet	18H	ROAr-*t*-C_4H_9

Table 3.15 ^{1}H-NMR analysis of (6a)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
7.24 - 7.16	multiplet	4H	H_a and H_b
7.02	singlet	4H	HOAr**H**
6.89	triplet J = 7.4 Hz	2H	H_c
6.79	doublet J = 6.7 Hz	2H	H_d
6.65	singlet	4H	ROAr**H**
6.34	singlet	2H	N**H**
4.40 , 4.22	2 singlet	8H	O**C**H_2**C**H_2O
4.35 , 3.24	2 doublet J = 13.2 Hz	8H	AB system Ar**C**$H_A$$H_B$Ar
3.83	singlet	4H	Ar**C**H_2NH
2.50	triplet J = 6.5 Hz	4H	N**C**H_2**C**H_2
1.42	multiplet	2H	CH_2**C**H_2**C**H_2
1.28	singlet	18H	HOAr-*t*-C_4**H**$_9$
0.84	singlet	18H	ROAr-*t*-C_4**H**$_9$

Table 3.17 ^{1}H-NMR analysis of (6c)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
7.24 - 7.14	multiplet	4H	H_a and H_b
7.03	singlet	4H	HOAr**H**
6.91-6.78	multiplet	4H	H_c, H_d
6.70	singlet	4H	ROAr**H**
4.44 , 3.24	2 doublet J = 13.2 Hz	8H	AB system ArCH_AH_BAr
4.36 , 4.29	2 singlet	8H	OCH_2CH_2O
3.82	singlet	4H	ArCH_2NH
2.49	singlet (broad)	4H	$CH_2NH_2CH_2$
2.38	singlet (broad)	2H	$ArCH_2NH_2CH_2$
1.28	singlet	18H	HOAr-*t*-C_4H_9
0.89	singlet	18H	ROAr-*t*-C_4H_9

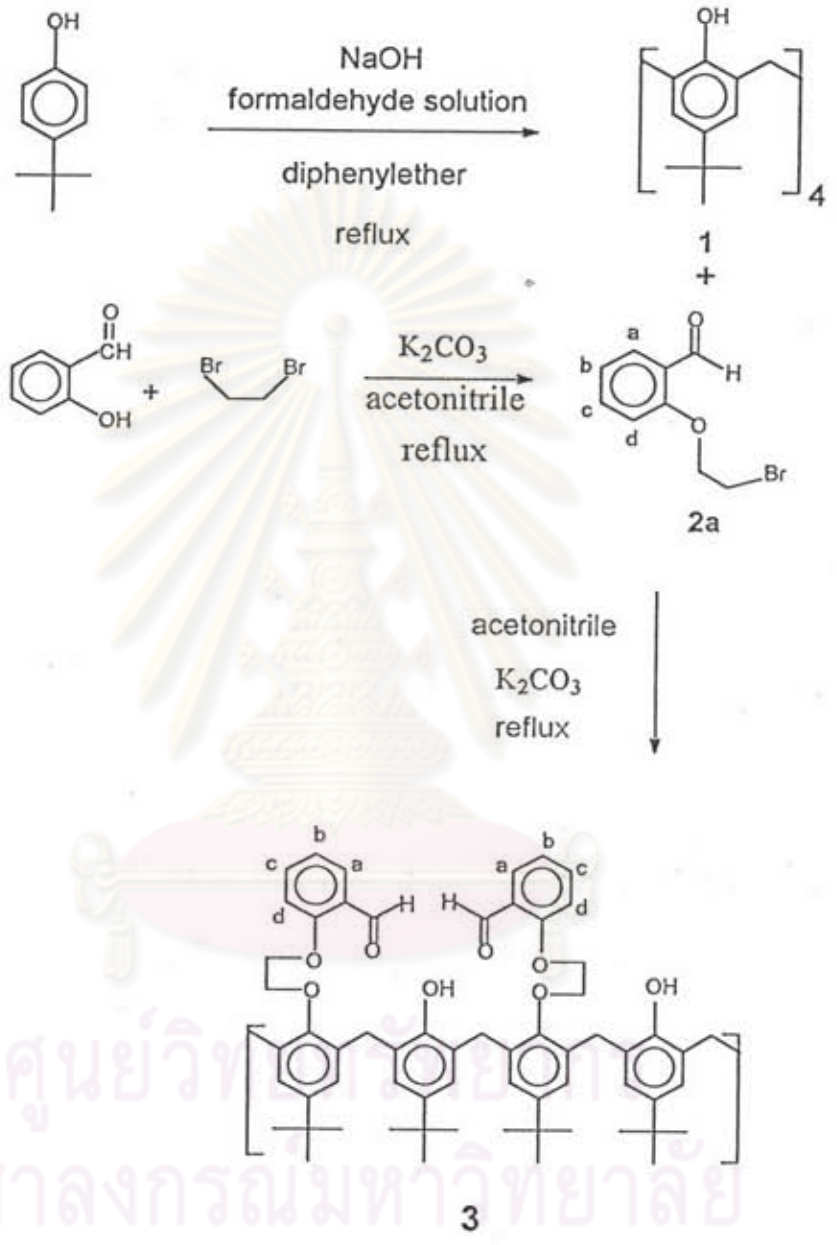
Table 3.18 ^{1}H-NMR analysis of (7a)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
7.50	doublet J = 7.1 Hz	2H	H_a
7.27	triplet J = 7.8 Hz	2H	H_b
7.24	singlet	4H	HOAr**H**
7.01- 6.92	multiplet	6H	H_c , H_d and ROAr**H**
4.84	singlet	4H	Ar**C**$\mathbf{H_2}$NH
4.48 , 4.32	singlet	8H	O**C**$\mathbf{H_2}$**C**$\mathbf{H_2}$O
4.32 , 3.32	2 doublets J = 13.2 Hz	8H	AB system Ar**C**$\mathbf{H_A}\mathbf{H_B}$Ar
3.51	singlet	6H	O**C**$\mathbf{H_3}$
3.51	singlet	4H	N**C**$\mathbf{H_2}$CH$_2$
3.22	singlet	12H	N**C**$\mathbf{H_3}$
2.77	singlet (broad)	2H	NCH$_2$**C**$\mathbf{H_2}$CH$_2$
1.22	singlet	18H	HOAr-*t*-C$_4\mathbf{H_9}$
1.05	singlet	18H	ROAr-*t*-C$_4\mathbf{H_9}$

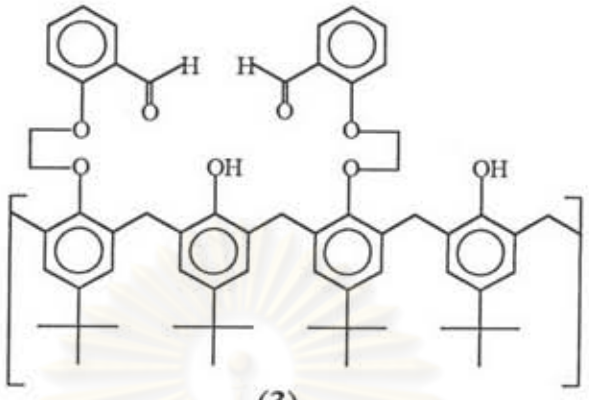
Table 3.19 ^{1}H-NMR analysis of (7b)

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
7.58-6.65	multiplet	16H	H_a , H_b HOAr**H** H_c, H_d and ROAr**H**
4.88	singlet (broad)	4H	Ar**C**$\mathbf{H_2}$NH
4.71	triplet J = 12.9 Hz	8H	N**C**$\mathbf{H_2}$N$\mathbf{H_2}$N
4.33	singlet	8H	O**C**$\mathbf{H_2}$**C**$\mathbf{H_2}$O
4.23 , 3.29	2 doublets J = 13.2 Hz	8H	AB system Ar**C**$\mathbf{H_A}$$\mathbf{H_B}$Ar
3.59	singlet	12H	O**C**$\mathbf{H_3}$, CH_2N^+(**C**$\mathbf{H_3}$)$_2$$CH_2$
3.29	singlet	12H	$ArCH_2N$(**C**$\mathbf{H_3}$)$_2$
2.50	singlet (broad)	8H	N**C**$\mathbf{H_2}$**C**$\mathbf{H_2}$
1.25	singlet	18H	HOAr-*t*-$C_4$$\mathbf{H_9}$
0.84	singlet	18H	ROAr-*t*-$C_4$$\mathbf{H_9}$

Scheme I



Scheme II

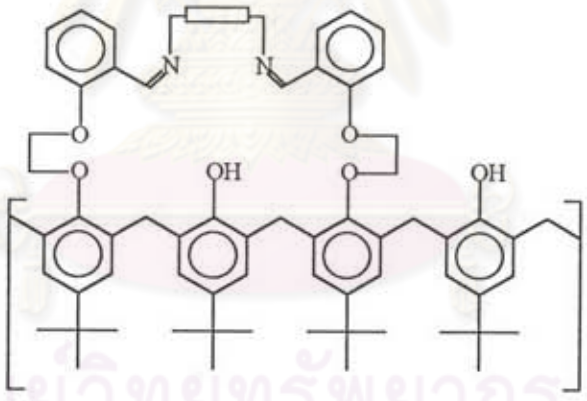


(3)

Primary diamine

Acetonitrile, Methanol

reflux 9 hours under nitrogen atmosphere



4(a-e)

 = $(CH_2)_3$ for (4a)

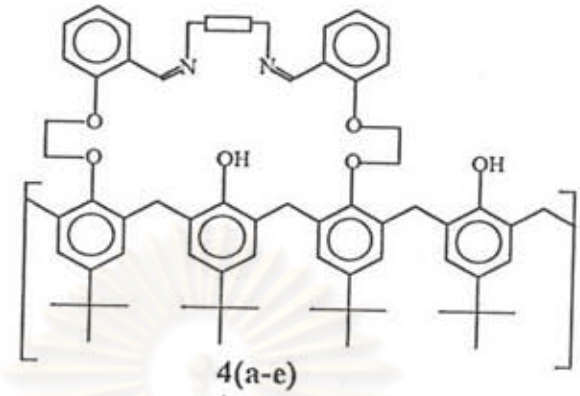
$(CH_2)_4$ for (4b)

$(CH_2CH_2NHCH_2CH_2)$ for (4c)

$(CH_2CH_2NHCH_2CH_2NHCH_2CH_2)$ for (4d)

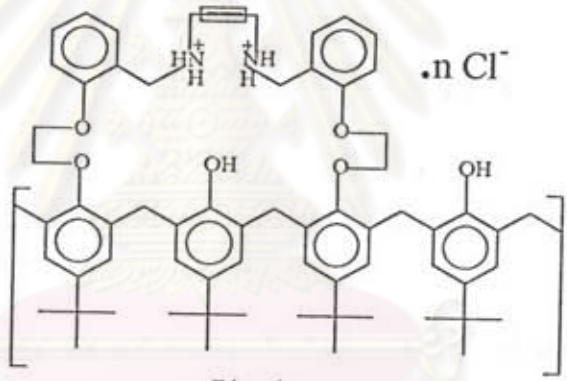
$(CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2)$ for (4e)

Scheme III



4(a-e)

1. $NaBH_4$ in dry THF (hydrogenation)
2. 0.7 % HCl in MeOH (acidification)



.n Cl^-

5(a-e)

 = $(CH_2)_3$ for (5a)

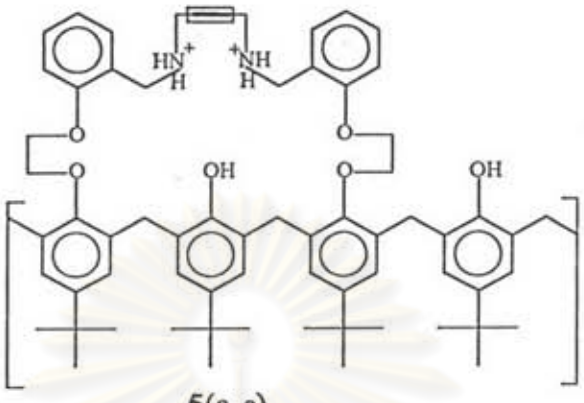
$(CH_2)_4$ for (5b)

$(CH_2CH_2\overset{+}{N}H_2CH_2CH_2)$ for (5c)

$(CH_2CH_2\overset{+}{N}H_2CH_2CH_2\overset{+}{N}H_2CH_2CH_2)$ for (5d)

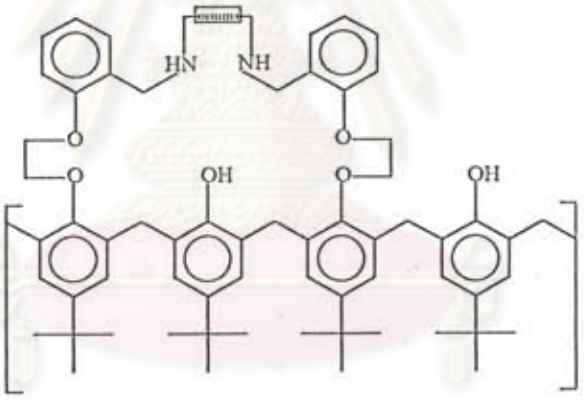
$(CH_2CH_2\overset{+}{N}H_2CH_2CH_2\overset{+}{N}H_2CH_2CH_2\overset{+}{N}H_2CH_2CH_2)$ for (5e)

Scheme IV



5(a-c)

NaOH
Methanol



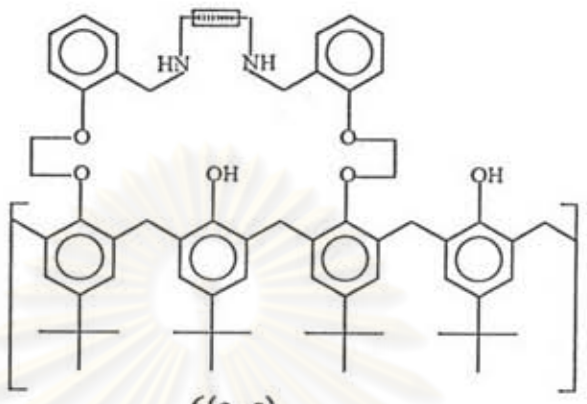
6(a-c)

 = $(CH_2)_3$ for (6a)

$(CH_2)_4$ for (6b)

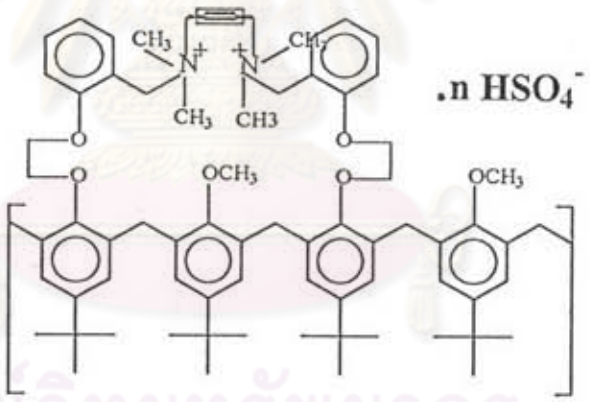
$(CH_2CH_2NHCH_2CH_2)$ for (6c)

Scheme V



6(a, c)

1. Methyliodide
   Acetonitrile , reflux
2. Dimethylsulfate
   Acetonitrile, reflux



.n HSO_4^-

7(a-b)

 = $(CH_2)_3$ for (7a)

$(CH_2CH_2\overset{+}{N}(CH_3)_2CH_2CH_2)$ for (7b)