Influence of alkali and alkaline earth ions on the *O*-alkylation of the lower rim phenolic-OH groups of *p-tert*-butyl-calix[4]arene to result in amide-pendants: Template action of K⁺ and the structure of K⁺ bound tetra-amide derivative crystallized with a *p-tert*-butyl-calix[4]arene anion

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Abstract. Role of alkali and alkaline earth ions on the formation of calix[4]arene-amide derivatives through *O*-alkylation of the lower rim phenolic-OH groups in general and template action of K⁺ in particular have been explored. Na⁺ and K⁺ ions among alkali, and Ca²⁺ and Sr²⁺ ions among alkaline earth have shown tetra-amide derivatives bound to metal ion species. Among all these, potassium salts act as template and yields a K⁺ bound tetra-amide derivative where the charge is counter balanced by a calix[4]arene-monoanion and the product is crystallographically characterized. Change in the amide precursor used in these *O*-alkylation reactions has no effect on the type of the amide derivative formed. Also demonstrated is a direct one-step reaction for the preparation of 1,3-di-amide derivative in high yield and low reaction period using CsHCO₃.

Keywords.   *O*-alkylation at the lower rim of calix[4]arene; template action of K⁺; mono-anion of *p-tert*-butyl-calix[4]arene; alkali and alkaline earth ions.

1. Introduction

Metal ion-directed derivatization of calixarenes would be an attractive proposition in building new calixarene based scaffolds since such methodology is expected to reduce the number of steps involved in the synthesis as well as improve the yields when compared to the conventional ones. Synthesis of the lower rim amide derivatives of calix[4]arene is not generally difficult and such derivatives are known and/or expected to complex alkali-, alkaline earth-,[1–9] lanthanide[10–13] and transition-[14–16] metal ions as reported in the literature. There are some reports in the literature regarding the synthesis of various types of calix[4]arene-amide derivatives which involve multi-step synthesis.[17,18] However, there has been no systematic study in the literature that utilizes the catalytic influence of metal ions in the derivatization of calix[4]arene. In this paper, we report for the first time, a systematic investigation of the role of alkali and alkaline earth metal ions (as their carbonates, bicarbonates, hydroxides, hydrides) on the different amide derivatives formed via *O*-alkylation at the lower rim of *p-tert*-butyl-calix[4]arene. Also this paper deals with the demonstration of the template action of K⁺ in forming tetra-amide derivative and its crystal structure determination that possesses monoanion of *p-tert*-butyl-calix[4]arene as counter ion.

2. Experimental

p-tert-Butyl-calix[4]arene, **1** was synthesized as per the reported procedure.[19] In case, the product is a mixture, individual products were separated either by column chromatography on silica gel or by fractional crystallization or by a combination of both these methods. After the separation, all the individual products were characterized by different techniques including FAB mass and NMR spectra (400 Mz,

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Varian) and the corresponding data is listed in this section.

2.1 *Preliminary crystallographic data for 9*

Crystals of **9** suitable for X-ray determination were obtained by dissolving the product in CH_3CN and allowing it to evaporate slowly at room temperature. Transparent single crystals of approximate dimensions $0.30 \times 0.10 \times 0.10$ mm^3 were selected on polarized microscope and mounted on a Bruker–Nonius κ-CCD diffractometer, Mo-K$_\alpha$ radiation (0.71073 Å). The structure was determined by direct methods and the refinement of atomic parameters based on full-matrix least squares on F^2 were performed using the SHELX-97 (Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998) programs. The crystallographic data is deposited at the Cambridge Crystallographic Data Centre with the CCDC code being 280392. Contacts for CCDC are, CCDC, 12 Union Road, CAMBRIDGE CB2 1EZ, UK; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/deposit.

2.2 *Synthesis and characterization data for the products*

2.2a *5,11,17,23-Tetra-tert-butyl-25-mono(N,N-diethyl aminocarbonyl)methoxy-26,27,28-trihydroxycalix[4] arene, (2):* 0.3 g NaH (60% oil) was taken in 3 neck round bottom flask and was washed several times with dried hexane. Calix[4]arene (1 g, 1.5 mmol) was taken in THF/DMF (40/8 mL) in another round bottom flask and stirred at 60°C for 1 h and then it was allowed to cool down to RT and the contents were transferred to the flask containing NaH and α-Cl-DMA (0.60 g, 4.5 mmol) and refluxed for 3 h and the reaction mixture was allowed to cool to RT and product formed was precipitated out by adding water into the reaction mixture. Crude product was isolated by filtration and separated by column chromatography on silica gel using ethylacetate/pet ether solvent system (10/90) to yield **2**, **3** and **4**. **2:** Yield 46%. m.p. 120–122°C. $C_{50}H_{67}NO_5 \cdot 2CH_3COO$ C_2H_5 (938.24): calc.: C 74.24, H 8.92, N 1.49; found: C 74.32, H 8.73, N 1.39%. FTIR: (KBr, cm^{-1}): 1653 ($v_{C=O}$), 3343 (v_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 7.08 (*s*, 2H, Ar-*H*), 7.04 (*s*, 2H, Ar-*H*), 6.95 (*d*, $J = 3.33$ Hz, 2H, Ar-*H*), 4.96 (*s*, 2H, OCH$_2$CO), 4.59 (*d*, $J = 12.82$ Hz, 2H, Ar-CH$_2$-Ar), 4.34 (*d*, $J = 13.55$ Hz, 2H, Ar-CH$_2$-Ar),

3.54 (*q*, $J = 7.33$, 6.96, 6.96 Hz, 2H, NCH$_2$), 3.39 (*d*, $J = 13.55$ Hz, 2H, Ar-CH$_2$-Ar), 3.37 (*d*, $J = 12.82$ Hz, 2H, Ar-CH$_2$-Ar), 3.27 (*q*, $J = 6.96$, 7.33, 6.96 Hz, 2H, NCH$_2$), 1.18 (*m*, 42H, C(CH$_3$)$_3$ and NCH$_2$CH$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 13.05, 14.15 (NCH$_2$CH$_3$), 29.75 (Ar–CH$_2$–Ar), 31.32, 31.50, 31.60 (C(CH$_3$)$_3$), 32.91, 33.14, 34.20, 33.95 (C(CH$_3$)$_3$), 40.41, 40.66 (NCH$_2$), 72.23 (OCH$_2$), 125.61, 125.86, 126.31 (C$_m$), 127.93 (*d*), 128.33, 134.02 (C$_o$), 142.84, 143.05, 147.79 (C$_p$), 148.27, 148.66, 151.99 (C$_i$), 168.44 (C=O). FAB-MS: *m/z* (intensity (%), fragment) 761 (70, [M–H$^+$]$^+$).

2.2b *5,11,17,23-Tetra-tert-butyl-25,27-bis(N,N-diethyl aminocarbonyl)methoxy-26,28-dihydroxycalix[4] arene, (3):* Yield 5%. m.p. > 240°C (decomp). $C_{56}H_{78}N_2O_6$ (875.23): calc.: C 76.85, H 8.98, N 3.20; found: C 76.60, H 8.79, N 3.35%. FTIR: (KBr, cm^{-1}): 1661 ($v_{C=O}$), 3366 (v_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 6.89 (*s*, 4H, Ar-H), 6.86 (*s*, 4H, Ar-H), 4.82 (*s*, 4H, OCH$_2$CO), 4.45 (*d*, $J = 12.82$ Hz, 2H, Ar-CH$_2$-Ar), 3.45 (*q*, $J = 6.96$, 6.96, 6.59 Hz, 8H, NCH$_2$), 3.27 (*d*, $J = 13.19$ Hz, 4H, Ar-CH$_2$-Ar), 1.18 (*m*, 30H, C(CH$_3$)$_3$ and NCH$_2$CH$_3$), 1.036 (*s*, 18H, C(CH$_3$)$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 13.04, 14.36 (NCH$_2$CH$_3$), 29.77 (Ar–CH$_2$–Ar), 31.21, 31.64 (C(CH$_3$)$_3$), 33.76, 33.99 (C(CH$_3$)$_3$), 40.32, 41.30 (NCH$_2$), 73.58 (OCH$_2$), 124.93, 125.68 (C$_m$), 127.82, 133.28 (C$_o$), 141.23, 146.84 (C$_p$), 150.12, 151.99 (C$_i$), 167.96 (C=O). FAB-MS: *m/z* (intensity (%), fragment) 875 (100, [M]$^+$).

2.2c *5,11,17,23-Tetra-tert-butyl-25,26-bis(N,N-diethylaminocarbonyl)methoxy-27,28-dihydroxycalix[4] arene, (4):* Yield 36%. m.p. 213–216°C. $C_{56}H_{78}N_2O_6 \cdot H_2O$ (893.23): C 75.03, H 9.40, N 4.02; found: C 75.30, H 9.22, N 3.85%. FTIR: (KBr, cm^{-1}): 1645 ($v_{C=O}$), 3343 (v_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 6.91 (*d*, $J = 2.19$ Hz, 2H, Ar-H), 6.86 (*d*, $J = 2.19$ Hz, 2H, Ar-H), 6.78 (*dd*, $J = 2.56$, 2.19 Hz, 4H, Ar-H), 5.27 (*d*, $J = 14.65$ Hz, 2H, OCH$_2$CO), 4.88 (*d*, $J = 13.91$ Hz, 1H, Ar-CH$_2$-Ar), 4.67 (*d*, $J = 14.65$ Hz, 2H, OCH$_2$CO), 4.65 (*d*, $J = 12.81$ Hz, 2H, Ar-CH$_2$-Ar), 4.32 (*d*, $J = 13.55$ Hz, 1H, Ar-CH$_2$-Ar), 3.35 (*m*, 8H, NCH$_2$), 3.23 (*dd*, $J = 13.92$, 12.82 Hz, 4H, Ar-CH$_2$-Ar), 1.20 (*m*, 36H, C(CH$_3$)$_3$ and NCH$_2$CH$_3$), 1.01 (*s*, 18H, C(CH$_3$)$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 13.08, 14.21 (NCH$_2$CH$_3$), 29.74 (Ar–CH$_2$–Ar), 31.29, 31.59 (C(CH$_3$)$_3$), 32.01 (*d*), 33.73, 33.89 (C(CH$_3$)$_3$), 40.27, 40.91 (NCH$_2$), 73.34 (OCH$_2$), 124.88, 125.03, 125.51 (C$_m$), 126.01, 127.24, 127.57

(C_o), 132·89, 134·04, 141·21 (C_p), 145·91, 149·06, 154·25 (C_i), 169·36 (C=O). FAB–MS: *m/z* (intensity (%), fragment) 875 (70, [M]$^+$).

2.2d *5,11,17,23-Tetra-tert-butyl-25,26,27,28- tetra-kis(N,N-diethylaminocarbonyl) methoxycalix[4]arene, (5):* Yield 90%. m.p. 170–175°C. FTIR: (KBr, cm^{-1}): 1661 ($\nu_{C=O}$), 3440 (ν_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 6·81 (*s*, 8H, Ar-H), 5·20 (*d*, *J* = 12·2 Hz, 4H, Ar–CH$_2$–Ar), 5·02 (*s*, 8H, OCH$_2$CO), 3·35 (*m*, 16H, NCH$_2$), 3·20 (*d*, *J* = 12·21 Hz, 4H, Ar–CH$_2$–Ar), 1·14 (*m*, 60H, C(CH$_3$)$_3$ and NCH$_2$CH$_3$). FAB–MS: *m/z* (intensity (%), fragment) 1102 (100, [M]$^+$).

2.2e *[(5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-kis(N,N-diethylaminocarbonyl) methoxycalix[4]arene) sodium(I)]hydroxide, (6):* A mixture of **1** and NaOH or NaHCO$_3$ (1:5) was stirred at RT in dry CH$_3$CN. To this, α-Cl-DMA (5 eq to **1**) was added and reaction mixture was refluxed for 36 h. The reaction mixture was then allowed to cool down to RT, filtered through celite and the filtrate was evaporated under vacuum to result in a solid product. Yield 85%. m.p. >240°C (decomp.). C$_{68}$H$_{100}$N$_4$O$_8$NaOH. H$_2$O (1159·66): C 70·43, H 8·95, N 4·83, Na 1·98; found: C 70·30, H 9·02, N 4·85, Na 1·95%. FTIR: (KBr, cm^{-1}): 1656 ($\nu_{C=O}$), 3430 (ν_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 7·15 (*s*, 8H, Ar-H), 4·52 (*s*, 8H, OCH$_2$CO), 4·43 (*d*, *J* = 12·21 Hz, 4H, Ar–CH$_2$–Ar), 3·42 (*q*, *J* = 6·10, 7·33, 7·33, 8H, NCH$_2$), 3·32 (*d*, *J* = 12·21 Hz, 4H, Ar–CH$_2$–Ar), 3·17 (*q*, *J* = 6·09, 7·33, 7·43, 8H, NCH$_2$), 1·14 (*m*, 60H, C(CH$_3$)$_3$ and NCH$_2$CH$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 12·80, 14·04 (NCH$_2$CH$_3$), 30·02 (Ar–CH$_2$–Ar), 31·17 (C(CH$_3$)$_3$), 34·19 (C(CH$_3$)$_3$), 40·13, 40·54 (NCH$_2$), 73·98 (OCH$_2$), 125·64 (C_m), 134·82 (C_o), 134·34 (C_p), 148·13 (C_i), 167·95 (C=O). FAB–MS: *m/z* (intensity (%), fragment) 1125 (100, [M]$^+$).

2.2f *[(5,11,17,23-tetra-tert-butyl-25,26,27,28-tetra-kis(N,N-diethylaminocarbonyl) methoxycalix[4]arene) potassium(I)]hydroxide, (7):* This was synthesized by the same procedure as described for **6**, but using KHCO$_3$ in place of NaHCO$_3$. Yield 85%. m.p. 190–195°C. C$_{68}$H$_{100}$N$_4$O$_8$KOH·H$_2$O (1174·66): C 69·47, H 8·83, N 4·77, K 3·33; found: C 69·30, H 8·92, N 4·88, K 3·55%. FTIR: (KBr, cm^{-1}): 1654 ($\nu_{C=O}$), 3430 (ν_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 7·13 (*s*, 8H, Ar-H), 4·69 (*m*, 12H, OCH$_2$CO and Ar–CH$_2$–Ar), 3·44 (*q*, *J* = 5·19, 5·19, 6·72, 8H, NCH$_2$), 3·32 (*d*, *J* = 12·22 Hz, 4H, Ar–CH$_2$–Ar), 3·18 (*q*, *J* = 5·19,

5·32, 6·82, 8H, NCH$_2$), 1·19 (*m*, 60H, C(CH$_3$)$_3$ and NCH$_2$CH$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 12·82, 14·08 (NCH$_2$CH$_3$), 29·27 (Ar–CH$_2$–Ar), 31·47 (C(CH$_3$)$_3$), 34·02 (C(CH$_3$)$_3$), 40·42, 40·98 (NCH$_2$), 73·39 (OCH$_2$), 125·65 (C_m), 134·45 (C_o), 134·34 (C_p), 147·28 (C_i), 167·77 (C=O). FAB–MS: *m/z* (intensity (%), fragment) 1141 (100, [M]$^+$).

2.2g *[(5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis (N,N-diethylaminocarbonyl) methoxy-calix[4] arene)sodium(I)] 5,11,17,23-tetra-tert-butyl-25, 26, 27, 28-tetra hydroxycalix[4]arene-monoanion, (8):* This was synthesized by the same procedure as described for **6**, but using Na$_2$CO$_3$ in place of NaHCO$_3$. Resultant product was isolated and purified by fractional crystallization to yield **5** and **8**. The characterization details for **5** are given earlier in this experimental part. The details for **8** are: Yield 35%. m.p. >175°C (decomp.). C$_{112}$H$_{156}$N$_4$O$_{12}$Na.5CH$_3$CN (1978·71): C 74·05, H 8·71, N 6·37; Found: C 74·16, H 9·01, N 6·42%. FTIR: (KBr, cm^{-1}): 1658 ($\nu_{C=O}$), 3429 (ν_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 7·18 (*s*, 8H, Ar-H), 6·95 (*s*, 8H, Ar-H), 4·99 (*m*, 16H, OCH$_2$CO and Ar-CH$_2$-Ar), 4·42 (*d*, *J* = 12·21 Hz, 4H, Ar–CH$_2$–Ar), 3·42 (*q*, *J* = 7·33, 6·10, 7·33 Hz, 8H, NCH$_2$), 3·31 (*d*, *J* = 12·21 Hz, 4H, Ar–CH$_2$–Ar), 3·22 (*d*, *J* = 12·21 Hz, 4H, Ar-CH$_2$–Ar), 3·16 (*q*, *J* = 6·11, 7·32, 7·33 Hz, 8H, NCH$_2$), 1·19 (*m*, 96H, C(CH$_3$)$_3$ and NCH$_2$CH$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 13·07, 14·17 (NCH$_2$CH$_3$), 30·13 (Ar–CH$_2$–Ar), 31·29, 31·39 (C(CH$_3$)$_3$), 32·58, 34·01 (C(CH$_3$)$_3$), 40·23, 40·62 (NCH$_2$), 74·11 (OCH$_2$), 125·71, 125·93 (C_m), 127·69, 127·97 (C_o), 134·94, 146·64 (C_p), 158·35, 151·30 (C_i), 167·95 (C=O). FAB–MS: *m/z* (intensity (%), fragment) 1124 (100, [M-Calix[4] arenemonoanion]$^+$).

2.2h *[(5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-kis (N,N-diethylaminocarbonyl) methoxycalix[4]arene) potassium(I)] 5,11,17,23-tetra-tert-butyl-25, 26, 27, 28-tetrahydroxycalix[4]arene-monoanion, (9):* This was synthesized by the same procedure as described for **6**, but using K$_2$CO$_3$ in place of NaHCO$_3$. Yield 77%. m.p. >185°C (decomp.). C$_{112}$H$_{156}$N$_4$O$_{12}$K· 5CH$_3$CN (1994·82): C 73·46, H 8·64, N 6·32; found: C 73·16, H 9·01, N 6·52%. FTIR: (KBr, cm^{-1}): 1650 ($\nu_{C=O}$), 3429 (ν_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 13·17 (*br*, 3H, Ar-OH, D$_2$O exchanged), 7·15 (*s*, 8H, Ar–H), 6·92 (*s*, 8H, Ar-H), 4·57 (*m*, 16H, OCH$_2$CO and Ar–CH$_2$–Ar), 3·43 (*q*, *J* = 6·96, 7·33, 6·96 Hz, 8H, NCH$_2$), 3·325 (*d*, *J* = 12·45 Hz, 4H, Ar–CH$_2$–Ar),

3·18 (*m*, 12H, NCH$_2$ and Ar–CH$_2$–Ar), 1·20 (*m*, 96H, C(CH$_3$)$_3$ and NCH$_2$CH$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 13·08, 14·21 (NCH$_2$CH$_3$), 29·41 (Ar–CH$_2$–Ar), 31·38, 31·78 (C(CH$_3$)$_3$), 33·69, 34·22 (C(CH$_3$)$_3$), 40·70, 41·15 (NCH$_2$), 73·54 (OCH$_2$), 124·59, 125·78 (C$_m$), 130·35, 134·61 (C$_o$), 139·24, 147·34 (C$_p$), 151·31, 153·07 (C$_i$), 167·95 (C=O). FAB-MS: *m/z* (intensity (%), fragment) 1786 (3, [M]$^+$), 1141 (100, [M-calix[4]arene-monoanion]$^+$).

2.2i *[(5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-kis (N,N-diethylaminocarbonyl) methoxycalix[4] arene)calcium(II)]hydroxide, (10):* This was synthesized by the same procedure as described for **6**, but using Ca(OH)$_2$ in place of NaHCO$_3$. Yield 80%. m.p. >200°C (decomp.). C$_{68}$H$_{100}$N$_4$O$_8$Ca(OH)$_2$·CH$_3$CN (1215·74): C 69·10, H 8·70, N 5·76, Ca 3·29; found: C 69·30, H 8·65, N 5·98, Ca 3·45%. FTIR: (KBr cm^{-1}): 1632 ($\nu_{C=O}$), 3420 (ν_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 7·17 (*s*, 8H, Ar–H), 4·96 (*s*, 8H, OCH$_2$CO), 4·29 (*d*, *J* = 13·55 Hz, 4H, Ar–CH$_2$–Ar), 3·41 (*m*, *J* = 5·19, 5·19, 6·72, 20H, NCH$_2$ and Ar–CH$_2$–Ar) 1·16 (*m*, 60H, C(CH$_3$)$_3$ and NCH$_2$CH$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 12·77, 13·83 (NCH$_2$CH$_3$), 31·08 (Ar–CH$_2$–Ar), 31·29 (C(CH$_3$)$_3$), 34·23 (C(CH$_3$)$_3$), 41·46, 42·07 (NCH$_2$), 76·84 (OCH$_2$), 126·54 (C$_m$), 133·51 (C$_o$), 134·18 (C$_p$), 148·90 (C$_i$), 169·19 (C=O). FAB–MS: *m/z* (intensity (%), fragment) 1140 (25, [M-H]$^+$).
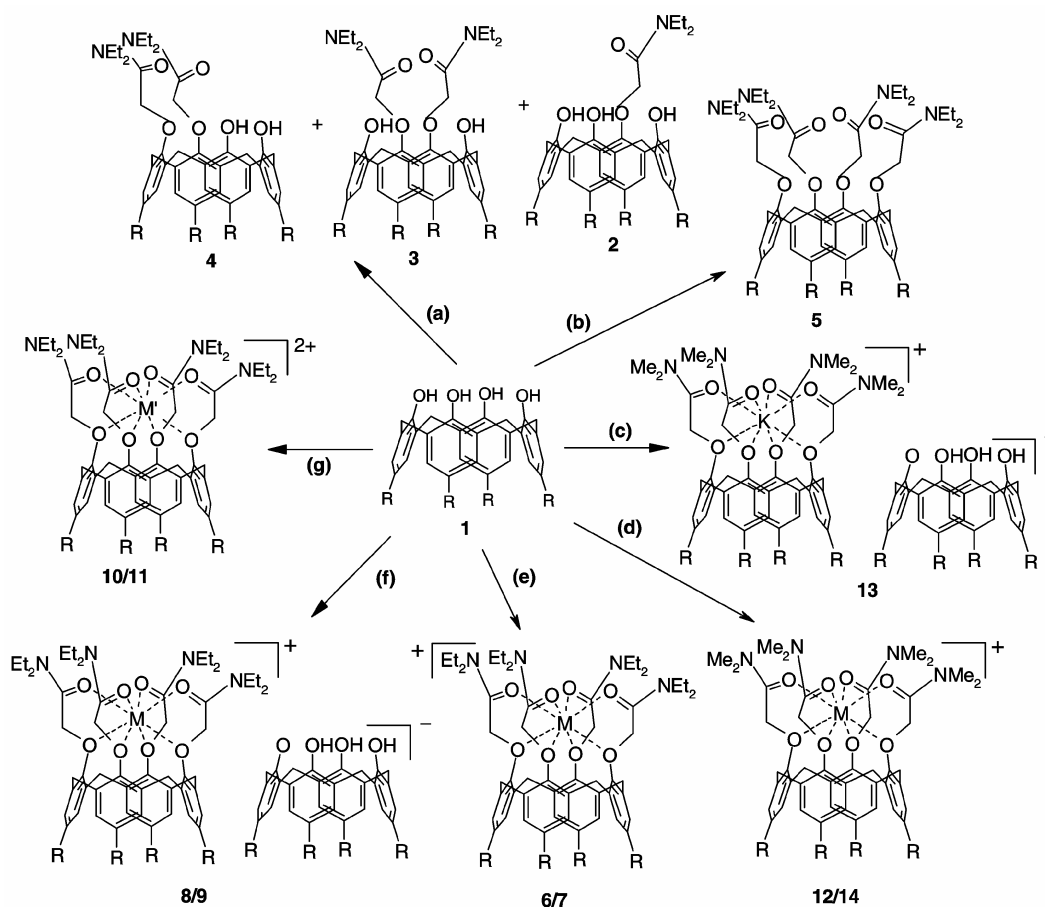
2.2j *[(5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-kis (N,N-diethylaminocarbonyl) methoxycalix[4] arene)strontium(II)]hydroxide, (11):* This was synthesized by the same procedure as described for **6**, but using Sr(OH)$_2$ in place of NaHCO$_3$. Yield 80%. m.p. >175°C (decomp). C$_{68}$H$_{100}$N$_4$O$_8$Sr(OH)$_2$·CH$_3$CN (1263·69): C 65·50, H 8·37, N 5·54, Sr 6·93; found: C 65·30, H 8·55, N 5·88, Sr 6·75%. FTIR: (KBr, cm^{-1}): 1635 ($\nu_{C=O}$), 3420 (ν_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 7·21 (*s*, 8H, Ar–H), 4·93 (*s*, 8H, OCH$_2$CO), 4·32 (*d*, *J* = 12·79 Hz, 4H, Ar–CH$_2$–Ar), 3·44 (*m*, *J* = 5·19, 5·19, 6·72, 20H, NCH$_2$ and Ar–CH$_2$–Ar) 1·16 (*m*, 60H, C(CH$_3$)$_3$ and NCH$_2$CH$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 12·89, 13·87 (NCH$_2$CH$_3$), 31·16 (Ar–CH$_2$–Ar), 31·43 (C(CH$_3$)$_3$), 34·32 (C(CH$_3$)$_3$), 41·46, 42·05 (NCH$_2$), 76·85 (OCH$_2$), 126·42 (C$_m$), 127·70 (C$_o$), 134·52 (C$_p$), 148·99 (C$_i$), 169·19 (C=O). FAB-MS: *m/z* (intensity (%), fragment) 1188 (25, [M]$^+$).

2.2k *[(5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-kis (N,N-dimethylaminocarbonyl) methoxycalix[4]*

arene)sodium(I)]Hydroxide (12): This was synthesized by the same procedure as described for **6**, but using α-Cl-DMA in place of α-Cl-DEA. Yield 87%. m.p. >185°C (decomp). C$_{60}$H$_{84}$N$_4$O$_8$NaOH·H$_2$O (1046·63): C 68·81, H 8·37, N 5·35, Na 2·20; found: C 68·53, H 8·53, N 5·68, Na 2·51%. FTIR: (KBr, cm^{-1}): 1657 ($\nu_{C=O}$), 3425 (ν_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 7·18 (*s*, 8H, Ar–H), 4·63 (*s*, 8H, OCH$_2$CO), 4·57 (*d*, *J* = 12·43 Hz, 4H, Ar–CH$_2$–Ar), 3·30 (*d*, *J* = 12·07 Hz, 4H, Ar–CH$_2$–Ar), 3·05, 2·92 (*s*, 12H each, NCH$_3$), 1·18 (*s*, 36H, C(CH$_3$)$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 30·22 (Ar–CH$_2$–Ar), 31·39 (C(CH$_3$)$_3$), 34·30 (C(CH$_3$)$_3$), 35·43, 35·80 (NCH$_3$), 73·93 (OCH$_2$), 125·82 (C$_m$), 134·96 (C$_o$), 148·17 (C$_p$), 151·01 (C$_i$), 169·16 (C=O). FAB–MS: *m/z* (intensity (%), fragment) 1012 (100, [M]$^+$).

2.2l *[(5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-kis (N,N-dimethylaminocarbonyl) methoxycalix[4] arene)potassium(I)]5,11,17,23-tetra-tert-butyl-25, 26, 27, 28-tetrahydroxycalix[4]arene-monoanion, (13):* This was synthesized by the same procedure as described for **12**, but using K$_2$CO$_3$ in place of Na-HCO$_3$. Yield 87%. m.p. >185°C (decomp). C$_{104}$H$_{140}$N$_4$O$_{12}$K (1676·01): C 74·47, H 8·41, N 3·34, K 2·33; Found: C 74·16, H 8·21, N 3·42, K 2·54%. FTIR: (KBr, cm^{-1}): 1659 ($\nu_{C=O}$), 3420 (ν_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 7·18 (*s*, 8H, Ar–H), 6·94 (*s*, 8H, Ar–H), 4·63 (*s*, 8H, OCH$_2$CO), 4·57 (*d*, *J* = 12·43 Hz, 4H, Ar–CH$_2$–Ar), 4·51 (*d*, *J* = 12·06 Hz, 4H, Ar–CH$_2$–Ar), 3·30 (*d*, *J* = 12·07 Hz, 4H, Ar–CH$_2$–Ar), 3·19 (*d*, *J* = 12·22 Hz, 4H, Ar–CH$_2$–Ar), 3·05, 2·92 (*s*, 12H each, NCH$_3$), 1·18 (*m*, 72H, C(CH$_3$)$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 29·59, 30·95 (Ar–CH$_2$–Ar), 31·55, 32·09 (C(CH$_3$)$_3$), 33·90, 35·45 (C(CH$_3$)$_3$), 35·74, 36·01 (NCH$_3$), 72·03 (OCH$_2$), 125·44, 125·90 (C$_m$), 133·66, 134·54 (C$_o$), 144·66, 147·44 (C$_p$), 151·51, 153·52 (C$_i$), 170·14 (C=O). FAB-MS: *m/z* (intensity (%), fragment) 1029 (25, [M-calix[4]arene-monoanion+H]$^+$).

2.2m *[(5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-kis(N,N-dimethylaminocarbonyl) methoxycalix[4]arene) potassium(I)]hydroxide, (14):* This was synthesized by the same procedure as described for **12**, but using KHCO$_3$ in place of NaHCO$_3$. Yield 80%. m.p. >200°C (decomp.). C$_{60}$H$_{84}$N$_4$O$_8$KOH·H$_2$O (1062·26): C 67·76 H 8·25, N 5·27, K 3·68; found: C 67·33, H 8·54, N 5·58, K 3·59%. FTIR: (KBr, cm^{-1}): 1654 ($\nu_{C=O}$), 3430 (ν_{OH}). ^{1}H NMR: (CDCl$_3$, δ ppm): 7·15 (*s*, 8H, Ar–H), 4·55 (*s*, 8H, OCH$_2$CO), 4·49 (*d*,

Scheme 1. Reactions of *p-tert*-butyl-calix[4]arene, **1** with α-Cl-DEA or α-Cl-DMA in the presence of alkali or alkaline earth metal salts (a) NaH, THF + DMF, α-Cl-DEA (1 : 3 : 3), 2 h; (b) NaH, THF + DMF, α-Cl-DEA (1 : 8 : 8), 8 h; (c) K$_2$CO$_3$, CH$_3$CN, α-Cl-DMA (1 : 5 : 5), 36 h; (d) Na$_2$CO$_3$ or MHCO$_3$, CH$_3$CN, α-Cl-DMA (1 : 5 : 5), 36 h; (e) MOH or MHCO$_3$, CH$_3$CN, α-Cl-DEA (1 : 5 : 5), 36 h; (f) M$_2$CO$_3$, CH$_3$CN, α-Cl-DEA (1 : 5 : 5), 36 h; (g) CaH$_2$ or M$'$ (OH)$_2$, CH$_3$CN, α-Cl-DEA (1 : 5 : 5), 36 h. M = Na$^+$ (**6**, **8**, **12**) and K$^+$ (**7**, **9**, **13**, **14**); M$'$ = Ca^{2+} (**10**) and Sr^{2+} (**11**). The ratios given here corresponds to, **1**: base: α-Cl-DEA/α-Cl-DMA. All the reactions were carried out at refluxing conditions. Please refer to the table 1 in order to note all the products formed in the reaction.

J = 12·05, 4H, Ar–CH$_2$–Ar), 3·35 (*d*, J = 12·05 Hz, 4H, Ar–CH$_2$–Ar), 3·00, 2·94 (*s*, 12H each, NCH$_3$), 1·18 (*s*, 36H, C(CH$_3$)$_3$). ^{13}C NMR: (CDCl$_3$, δ ppm): 30·25 (Ar–CH$_2$–Ar), 31·42 (C(CH$_3$)$_3$), 33·72 (C(CH$_3$)$_3$), 34·32, 35·45 (NCH$_3$), 73·94 (OCH$_2$), 125·91 (C_m), 135·02 (C_o), 148·34 (C_p), 151·10 (C_i), 169·11 (C=O) FAB–MS: *m/z* (intensity (%), fragment) 1028 (100, [M]$^+$).

3. Results and discussion

3.1 *Role of alkali metal ions on the reaction between p-tert-butyl-calix[4]arene and α-chlorodiethylacet-amide (α-Cl-DEA)*

Reactions between the *p-tert*-butylcalix[4]arene, **1** and α-Cl-DEA were carried out in the presence of carbonates, bicarbonates and hydroxides of Li$^+$, Na$^+$, K$^+$, Rb$^+$ and Cs$^+$ in acetonitrile under N$_2$ atmosphere (scheme 1). The reactions of **1** and α-Cl-DEA in the presence of Li$^+$ salts yield no product and only the unreacted calix[4]arene was recovered even when the reaction periods were long (table 1).

Reaction of **1** and α-Cl-DEA in the presence of Na$_2$CO$_3$ in the ratio 1 : 2 : 2 for 20 h yielded mono-amide derivative (**2**) along with some unreacted **1** (table 1). However, when the same reaction was performed at 1 : 5 : 5 for a period of 36 h, a product mixture containing mono- (**2**), 1,3-di- (**3**) amide derivatives in addition to **8** were formed. Product **8** was separated from this mixture by fractional crystallization, and **2** and **3** were separated by chromatography. On the basis of ^{1}H and ^{13}C NMR spectra,

Table 1. Reactions carried out between **1** and α-Cl-DEA in the presence of alkali and alkaline earth salts and the products obtained.[#]

Entry number	Base	1 : Base: α-Cl-DEA	Reaction time (h)	Product(s) (yield, %)
1	Li_2CO_3	1 : 2 : 2; 1 : 5 : 5	20, 36	No product
2	Na_2CO_3	1 : 2 : 2*	20	**2** (20)
3		1 : 5 : 5	36	**2**(10), **3**(15), **8** (25)
4	K_2CO_3	1 : 2 : 2; 1 : 5 : 5	5, 10, 20 or 36	**9** (90)
5	Rb_2CO_3	1 : 2 : 2*	20	**2** (15)
6		1 : 5 : 5	36	**2** (15), **3** (23)
7	Cs_2CO_3	1 : 2 : 2*	20	**2** (18)
8		1 : 5 : 5	36	**5** (55)
9	$NaHCO_3$	1 : 2 : 2	20	**3** (10), **6** (27)
10		1 : 5 : 5	36	**6** (80)
11	$KHCO_3$	1 : 2 : 2*	20	**2** (12), **7** (35)
12		1 : 5 : 5	36	**7** (85)
13	$RbHCO_3$	1 : 2 : 2*	36	**3** (15)
14		1 : 5 : 5*	36	**3** (35)
15	$CsHCO_3$	1 : 3 : 3	36	**3** (80)
16		1 : 5 : 5	36	**3** (40), **5** (30)
17	LiOH	1 : 2 : 2; 1 : 5 : 5	20,36	No product
18	NaOH	1 : 2 : 2*	20	**2** (10), **3** (25), **6** (8)
19		1 : 5 : 5	36	**6** (82)
20	KOH	1 : 2 : 2*	20	**2** (10), **3** (25), **7** (10)
21		1 : 5 : 5	36	**7** (75)
22	RbOH*	1 : 2 : 2	20	**3** (25)
23		1 : 5 : 5	36	**3** (25), **5** (35)
24	CsOH*	1 : 2 : 2	20	**3** (30)
25		1 : 5 : 5	36	**3** (25), **5** (50)
26	NaH	1 : 3 : 3	2	**2** (15), **3** (55), **4** (5)
27		1 : 8 : 8	8	**5** (95)
28	$MgCO_3$*	1 : 2 : 2, 1 : 5 : 5	20, 36	No product
29	$CaCO_3$*	1 : 5 : 5, 1 : 10 : 10	20, 36	No product
30	$SrCO_3$*	1 : 5 : 5	20, 36	No product
31	$Mg(OH)_2$*	1 : 5 : 5	36	No product
32	$Ca(OH)_2$	1 : 2 : 2*	36	**2** (15), **10** (25)
33		1 : 5 : 5	36	**10** (77)
34	$Sr(OH)_2$	1 : 2 : 2*	20	**2** (5), **5**(10), **11** (15)
35		1 : 5 : 5	36	**11** (90)[-]
36	$Ba(OH)_2$	1 : 2 : 2*	20	**5** (20)
37		1 : 5 : 5	36	**5** (77)
38	CaH_2	1 : 5 : 5	36	**10** (84)

[#]Refer to the Scheme 1 for identity of products. *Unreacted calix[4]arene is present

8 was identified to be Na^+ bound calix[4]arene-tetramide where an additional calix[4]arene acts as counter anion. Similar reaction between **1** and α-Cl-DEA in the presence K_2CO_3 in 1 : 2 : 2 ratio for 20 h yielded a single product **9** that is analogous to **8** but K^+ is present in place of Na^+ and the structure of **9** was determined by single crystal X-ray diffraction as reported in this paper. The same product was obtained even when this reaction was repeated with 1 : 3 : 3, 1 : 3 : 5 and 1 : 5 : 5 ratios indicating that the charge of the monoanion of *p-tert*-butyl-calix[4]arene is counter-balanced by the K^+-

bound tetra-amide derivative, where the reaction is driven by the template action of K^+. However, 1 : 5 : 5 reaction carried out using either $MHCO_3$ or MOH (M = Na or K) resulted in a single product, **3** or **6** or **7**, a M^+ bound calix[4]arene-tetramide where the counter anion could not be identified based on ^{1}H NMR and hence rules out the presence of a calixarene based anion. On the other hand, FTIR spectra suggest the presence of OH^- species. The molecular ion peak in FAB mass spectra of **6** and **7** corresponds to a tetra-amide derivative bound to M^+. Thus, the mono-anion of calix[4]arene was formed only in the

case of carbonate and not with other anions and hence an anion dependency.

On the other hand, the reactions carried out in the presence of carbonate, bicarbonate and hydroxide salts of Rb^+ and Cs^+ always yielded a mixture of products including the unreacted **1**, whether these were carried out at lower or at higher ratios (table 1), with an exception noticed in case of $CsHCO_3$. Reaction between **1** and α-Cl-DEA in the presence of $CsHCO_3$ yielded a mixture of 1,3-di-(**3**) and tetra-(**5**) amide derivatives at $1:5:5$ ratio and only a single product, viz. 1,3-di-amide (**3**) derivative at $1:3:3$ ratio. In the literature,[20] it was reported to have been obtained **3** alone when the reaction was carried out in the presence of K_2CO_3 in $1:1:2$ ratio. However, the same reaction in our hands yielded a mixture of mono- (**2**) and 1,3-di- (**3**) -amide derivatives instead of the claimed **3** alone. Therefore, the formation of 1,3-di-amide derivative, **3** in the reaction of $CsHCO_3$ at $1:3:3$ is interesting and important as the same derivative has been synthesized in the literature by going through four-steps.[17] The literature procedure has several disadvantages besides the number of steps and effective low yields, such as, long reaction periods (4–5 days) and handling of corrosive (thionylchloride), carcinogenic (benzene) and unstable (diacid-chloride) substances or species. However, the procedure reported in this paper yields a pure product in as high as 80% yield in a single-step without the use of such hazardous chemicals and in just 1.5 days.

Reaction between **1** and α-Cl-DEA in presence of NaH in THF/DMF in the ratio of $1:3:3$ yielded a product[21] mixture of mono- (**2**), 1,3-di- (**3**) and 1,2-di- (**4**) amide derivatives (scheme 1 and table 1) as confirmed based on ^1H NMR. However, when the same reaction was carried out at a higher ratio, viz. $1:8:8$, only a single product, calix[4]arene-tetraamide (**5**) was obtained and this result is consistent with that reported in the literature.[22] Thus, among all the reactions reported in this paper only the NaH reaction leads to the formation of the 1,2-di-amide derivative.

3.2 *Role of alkaline earth metal ions on the reaction between p-tert-butyl-calix[4]arene and α-Cl-DEA*

While alkali carbonates were found to be active in these *O*-alkylation reactions (table 1) that of alkaline earth ones, Mg^{2+}, Ca^{2+} and Sr^{2+} were inactive either

at $1:2:2$ or at $1:5:5$ ratios. Similar is the case with the reactions of $Mg(OH)_2$. The reactions of CaH_2, and the hydroxides of Ca^{2+} and Sr^{2+} (diagonally related to Na^+ and K^+) resulted in the formation of M^{2+} bound tetra-amide derivatives, viz. **10** and **11** which are similar to 6 (Na^+) and 7 (K^+) but the bound metal ion is different. On the other hand, the $Ba(OH)_2$ reaction resulted in pure tetra-amide derivative (**5**) in high yields. The other high yield method reported in the literature[22] for synthesizing tetraamide is the reaction using NaH. Thus, the demonstration of the use of $Ba(OH)_2$ in making tetra-amide derivative in high yield is certainly adventitious as the corresponding synthetic procedure does not demand for handling NaH. Thus, it is evident from these results that among the alkaline earth metal ions, only Ca^{2+} and Sr^{2+} hydroxides were found to act as templates for the formation of M^{2+} bound calix[4]arene-tetra-amide derivatives.

3.3 *Role of alkali metal ions on the reaction between p-tert-butyl-calix[4]arene and α-chlorodimethylacetamide (α-Cl-DMA)*

Reaction between **1** and α-Cl-DMA in the presence of Na_2CO_3 and K_2CO_3 ($1:5:5$ ratio and 36 h, reflux) yielded **12** and **13** respectively in 85% yield. These are analogous to **6** and **9** obtained in case of α-Cl-DEA reaction. Under similar reaction conditions, $NaHCO_3$ and $KHCO_3$ gave compounds, **12** and **14** respectively in about 85% yield. These products are analogous to **6** and **7** obtained in case of α-Cl-DEA reaction, viz. M^+ bound tetra-amide derivative. Thus, the change in amide precursor from α-Cl-DEA to α-Cl-DMA did not bring any change in the type of amide derivative formed.

3.4 *Separation of individual products and characterization*

As can be seen from the table 1 that many reactions yield a mixture of products. TLC and ^1H NMR studies clearly indicated the presence of different products in these mixtures. However, the individual products were separated subsequently and were characterized by ^1H and ^{13}C NMR and FAB mass spectra. All the separated products have clearly shown satisfactory elemental and metal ion analyses. FTIR, NMR, MS and elemental data of all the compounds are presented in the experimental section.

3.4a *Identification of different amide derivatives:* ^{1}H and ^{13}C NMR spectra were measured in CDCl$_3$ for all the products. The spectra were consistent with the presence of cone conformation as deduced based on the bridged methylene group resonances.
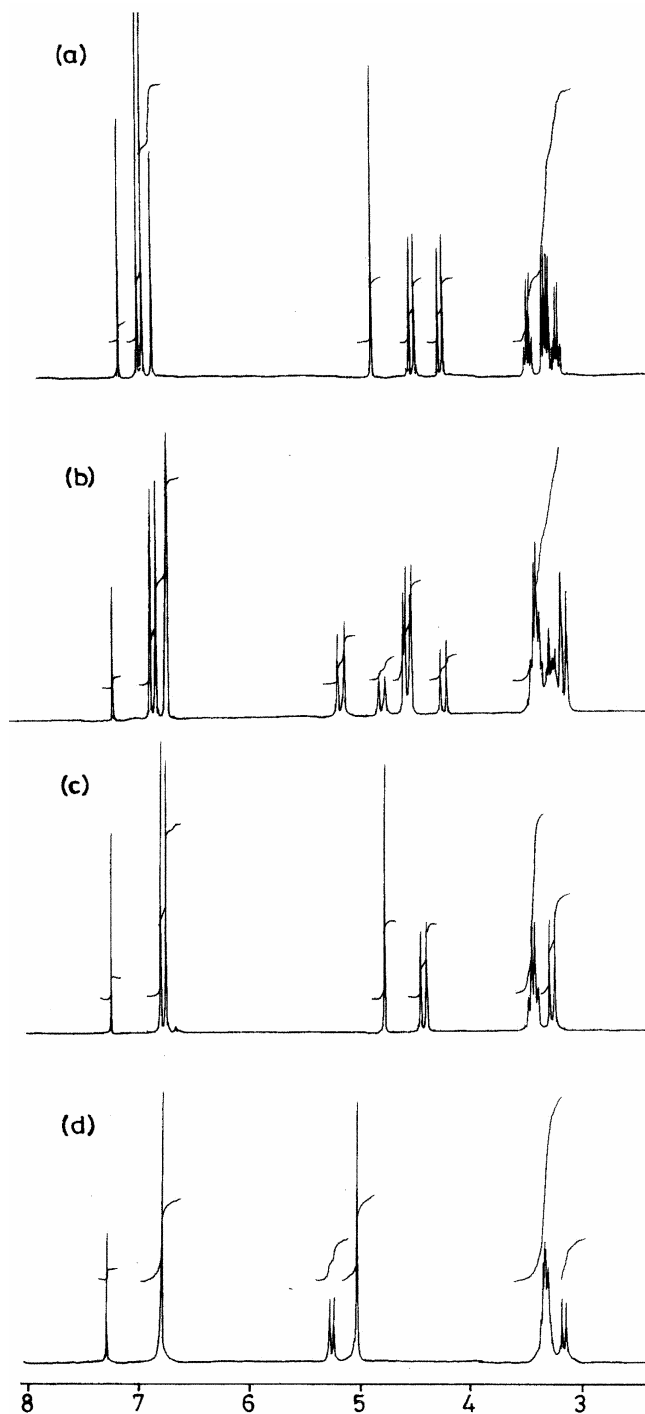
Two multiplets appeared at 1·05 and 3·33 ppm arising from methyl and methylene protons of –NCH$_2$CH$_3$ moiety respectively supported the presence of amide arms in these derivatives. The different calix[4] arene-amide derivatives can be easily differentiated based on –OCH$_2$ signals, viz. 4·96 (mono-), 4·67 (doublet, 1,2-di-), 4·82 (1,3-di-) and 5·02 (tetra-amide) as well as the aromatic signals, viz. mono- (three singlets), 1,2-di- (two doublets and one doublet of doublet), 1,3-di- (two singlets) and tetra- (one singlet) as can be seen from figure 1. In case of the spectra measured from the product mixture, the peak areas will provide an estimate of the amount of products formed.

3.4b *Identification of metal ion bound species:* In FTIR, ν_{CO} bands did not show any considerable shift in the tetra-amide bound to Na^{+} (**6** and **8**) or K^{+} (**7** and **9**) when compared to the corresponding bands in free derivative and hence cannot be used for identifying M^{+} binding. Changes observed in the ν_{OH} are reflective of the presence of OH^{-} counter ion in case of **8** and **9**. On the other hand, Ca^{2+} (**10**) and Sr^{2+}
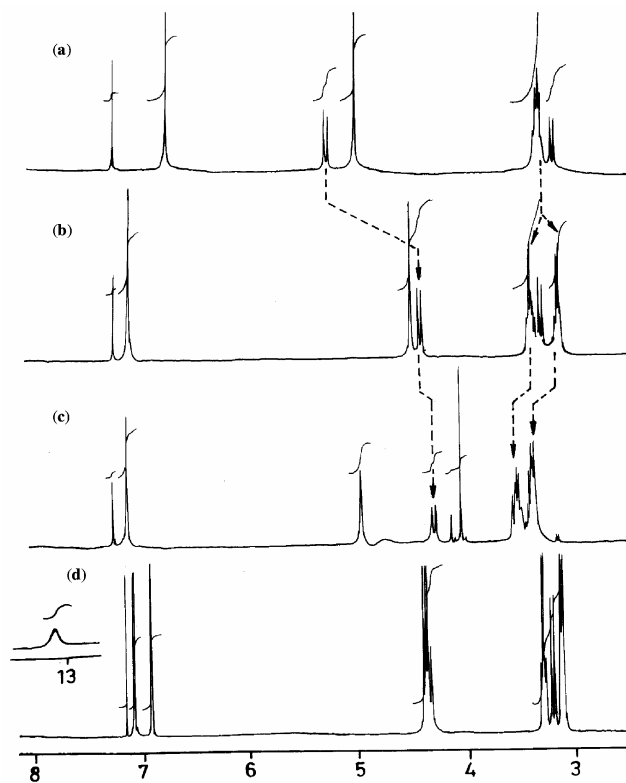

Figure 1. Comparison among ^{1}H NMR spectra of various calix[4]arene-amide derivatives: (**a**) **2** (mono); (**b**) **3** (1,3-di); (**c**) **4** (1,2-di) and (**d**) **5** (tetra).

Figure 2. Comparison among ^{1}H NMR spectra of calix[4]arene-tertra-amide (**a**) **5**; and its complexes, (**b**) **7** (K^{+}); (**c**) **10** (Ca^{2+}) and (**d**) **9** (K^{+}, along with calix[4] arene-monoanion).

Table 2. Crystal structure refinement parameters for **9**.

Empirical formula	$C_{119}H_{165.5}KN_{7.5}O_{12}$
Formula weight	1930·68
Temperature	150(2) K
Wavelength	0·71073 Å
Crystal system	Monoclinic
Space group	P_n
Unit cell dimensions	$a = 16·300(5)$
	$b = 21·518(5)$
	$c = 16·776(5)$Å
	$\beta = 102·76(2)°$
Volume	5739(3) Å^3
Z	2
Density (calculated)	1·117 mg/m^3
Absorption coefficient	0·107 mm^{-1}
F (000)	2091
Crystal size	$0·30 \times 0·10 \times 0·10$ mm^3
Theta range for data collection	3·46 to 26·37°
Index ranges	$-20 \le h \le 20, -26 \le k \le 26, -20 \le l \le 20$
Reflections collected	44101
Independent reflections	23060 [R(int) = 0·0267]
Completeness to theta	26·37° (99·7%)
Absorption correction	Semi-empirical
Max. and min. transmission	0·9894 and 0·9687
Data/restraints/parameters	23060/2/1293
Goodness-of-fit on F^2	1·032
Final R indices [$I > 2sigma(I)$]	$R1 = 0·0438, wR2 = 0·1071$
R indices (all data)	$R1 = 0·0533, wR2 = 0·1132$
Extinction coefficient	0·0049(4)
Largest diff. peak and hole	0·456 and −0·340 eÅ^{-3}

Table 3. Selected bond lengths (Å) and bond angles (°) of K$^+$ coordination sphere in **9**.

K(1)–O(8)	2·637(2)	K(1)–O(7)	2·698(2)
K(1)–O(10)	2·637(2)	K(1)–O(12)	2·710(2)
K(1)–O(5)	2·664(2)	K(1)–O(9)	2·717(2)
K(1)–O(6)	2·691(2)	K(1)–O(11)	2·813(2)
O(8)–K(1)–O(10)	126·3(1)	O(6)–K(1)–O(9)	130·7(1)
O(8)–K(1)–O(5)	79·3(1)	O(7)–K(1)–O(9)	148·0(1)
O(10)–K(1)–O(5)	60·5(1)	O(12)–K(1)–O(9)	136·6(1)
O(8)–K(1)–O(6)	77·1(1)	O(8)–K(1)–O(11)	71·7(1)
O(10)–K(1)–O(6)	154·3(1)	O(10)–K(1)–O(11)	134·5(1)
O(5)–K(1)–O(6)	123·1(1)	O(5)–K(1)–O(11)	150·1(1)
O(8)–K(1)–O(7)	123·4(1)	O(6)–K(1)–O(11)	57·3(1)
O(10)–K(1)–O(7)	82·8(1)	O(7)–K(1)–O(11)	125·0(1)
O(10)–K(1)–O(9)	74·9(1)	O(12)–K(1)–O(11)	85·2(1)
O(5)–K(1)–O(9)	71·8(1)	O(9)–K(1)–O(11)	86·8(1)

(11) bound tetra-amide derivatives have shown a shift in the carbonyl stretching frequency by about 29 and 24 cm^{-1} respectively. However, ^{1}H NMR spectra exhibited clear-cut differences among the tetra-amide **(5)** and its corresponding metal ion complexes **(6**, **7**, **8**, **9**, **10** and **11)** in the signals of bridged methylene and methylene of −NEt as shown in figure 2. In **8** and **9**, where the calix[4]arene-monoanion is present, the spectra showed two sets of calix[4]arene based signals where one set arises from metal bound tetra-amide and the other from calix[4]arene-mono-anion.
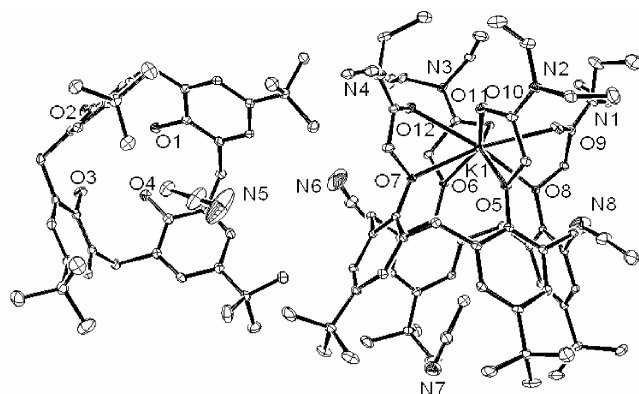
Figure 3. Crystal structure of **9** as ORTEP plot. The hetero-atoms are labelled for clarity. There are four aceto-nitrile molecules per unit cell.

3.5 *Crystal structure of* **9**

The data collection and refinement parameters for the crystal structure, **9** were listed in table 2. The molecular structure of **9** shown in figure 3 clearly indicates the presence two calix[4]arene units, of which one is an anionic and the other is K$^+$ bound tetraamide derivative. Important bond lengths and bond angles of the coordination sphere are summarized in table 3. In the cationic portion of the crystal structure of **9**, the *p-tert*-butyl-calix[4]arene is alkylated at all the four phenolic-*O*-centers by N,N-diethylacetamide moiety to result in a tetra-amide derivative. The K$^+$ ion is bound through eight oxygens of the tetra-amide, of which four were from the amide moieties and the remaining were from the lower rim pendant ether oxygens. Thus, the complex shows bond distances of K...O$_{ether}$, 2·637–2·698 Å and K...O$_{amide}$, 2·637–2·813 Å respectively. The geometry around K$^+$ fits well with a bi-capped octahedron. The counter anion in **9** exhibited a O...O (1,2-type) distances of 2·523, 2·538, 2·766 and 2·949, and O...O (1,3-type) distances of 3·610 and 3·936 consistent with a localized anion on the calix[4] arene moiety in the crystal structure and this data is comparable with the results reported in the literature.[23] Also comparison of this data with that found in case of the neutral *p-tert*-butyl-calix[4]arene structure[24] supports the presence of mono-anion in case of **9**.

There are four acetonitrile molecules present in the unit cell, of which, one was located close to the lower rim oxygens of the anion with partly being buried in the hydrophobic environment, another was completely buried in the cavity of calixarene of the cationic part and the remaining two were in the lattice. On the other hand, the K$^+$-complex of same *p-tert*-butyl-calix[4]arene-tetraamide with thiocyante or iodide counter anion was demonstrated where the pre-formed *p-tert*-butyl-calix[4]arene-tetraamide was simply reacted with the corresponding potassium salt,[21] viz. KSCN or KI and was not obtained from the reactions of the type reported in this paper. Thus, in the literature, the K$^+$ bound tetra-amide structure is known, and also known is the structure of the calix[4]arene anion but not these two together in the same compound. Thus, **9** reported in this paper is altogether unknown in the literature and the crystallographic characterization is definitely done for the first time as reported in this paper.

4. Conclusions

This paper clearly demonstrates the interactive role of alkali and alkaline earth salts on the formation of calix[4]arene-amide derivatives in general and template action of K$^+$ in particular, through *O*-alkylation at the lower rim. Among the alkali and alkaline earth ions studied, Li$^+$ and Mg^{2+} were completely non-reactive.

The Na$^+$ and K$^+$ drives the reaction to form their metal ion bound tetra-amide derivatives, so is the case with Ca^{2+} and Sr^{2+} owing to their diagonal relationship. Though the carbonates, hydroxides and hydrides of alkali salts are capable of producing metal ion bound tetra-amide, it is the carbonate only that drives the formation of calix[4]arene-monoanion. While Na$_2$CO$_3$ produces this compound along with other products, K$_2$CO$_3$ provides this as a single product. On the other hand, none of the Ca^{2+} and Sr^{2+} show any calix[4]arene-monoanion formation. Therefore, it is K$^+$ that acts as template in these reactions.

The larger ions such as Cs$^+$ and Ba^{2+} can only drive the reaction to the formation of tetra-amide but not to the metal ion bound ones, indicating the inability of these ions to act as templates owing to the size constraints posed by the binding core formed from the four pendants of the tetra-amide derivative. Hence the template action is dependent on the size of the ion as well. Thus, among all the salts studied, it is the K$_2$CO$_3$ that produces the K$^+$ bound tetra-amide while forming the calix[4]arene anion and no other combination could do this. Thus very small and very large ions were not effective in generating calix[4]arene monoanion along with the metal ion bound tetra-amide derivative.

1,3-Di-amide was reported to have been synthesized in the literature via four-steps with long reaction period where corrosive, carcinogenic and unstable species have to be handled. However, the present paper demonstrates a straight-forward one-step reaction that gives high yield with low reaction period using $CsHCO_3$.

Almost all the reactions carried out at a lower ratio $(1:2:2)$ yielded mono-amide derivative. Among all the reactions reported in this paper only the NaH reaction leads to the 1,2-di-amide derivative. None of the reactions reported in this paper yield tri-amide derivative. In order to synthesize tri-amide derivative a mixture of BaO and $Ba(OH)_2$ were used.[16]

The change in amide precursor, viz. α-Cl-DEA or α-Cl-DMA, has no effect on the type of amide derivatives formed and hence suggests the general nature of the reactions demonstrated in this paper.

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References

1. Arduini A, Giorgi G, Pochini A, Secchi A and Ugozzoli F 2001 *Tetrahedron* **57** 2411
2. Beer P D, Drew M G B, Gale P A, Leeson P B and Ogden M I 1994 *J. Chem. Soc., Dalton Trans.* 3479
3. Wolf N J, Georgiev E M, Yordanov A T, Whittlesey B R, Koch H F and Roundhill D M 1999 *Polyhedron* **18** 885
4. Moser A, Yap G P A and Detellier C 2002 *J. Chem. Soc., Dalton Trans.* 428
5. Bochenska M, Zielinska A, Kravtsov V C, Gdaniec M, Luks E and Radecka-Paryzek W 2002 *Polyhedron* **21** 763
6. Halouani H I, Dumazet-Bonnamour, Duchamp C, Bavoux C, Ehlinger N, Perrin M and Lamartine R 2002 *Eur. J. Org. Chem.* 4202
7. Casnati A, Baldini L, Pelizzi N, Rissanen K, Ugozzoli F and Ungaro R 2000 *J. Chem. Soc., Dalton Trans.* 3411
8. Casnati A, Barboso S, Rouquette H, Schwing-Weill M J, Arnaud-Neu F and Dozol J F 2001 *J. Am. Chem. Soc.* **123** 12182
9. Muzet N, Wipff G, Casnati A, Domiano L, Ungaro R and Ugozzoli F 1996 *J. Chem. Soc. Perkin Trans.* **2** 1065
10. Beer P D, Drew M G B, Kan M, Leeson P B, Ogden M I and Williams G 1996 *Inorg. Chem.* **35** 2202
11. Beer P D, Drew M G B and Ogden M I 1997 *J. Chem. Soc., Dalton Trans.* 1489
12. Beer P D, Drew M G B, Leeson P B and Ogden M I 1996 *Inorg. Chim. Acta* **246** 133
13. Beer P D, Drew M G B, Grieve A and Ogden M I 1995 *J. Chem. Soc., Dalton Trans.* 3455
14. Arnaud-Neu F, Barrett G, Corry D, Cremin S, Ferguson G, Gallagher J F, Harris S J, McKervey M A and Schwing-Weill M J 1997 *J. Chem. Soc. Perkin Trans.* **2** 575
15. Beer P D, Drew M G B, Leeson P B and Ogden M I 1995 *J. Chem. Soc., Dalton Trans.* 1273
16. Ogden M I, Skelton B W and White A H 2001 *J. Chem. Soc., Dalton Trans.* 3073
17. Collins E M, McKervey M A, Madigan E, Moran M B, Owens M, Ferguson G and Harris S J 1991 *J. Chem. Soc., Perkin Trans.* **1** 3137
18. Rao P V, Rao C P, Kolehmainen E, Wegelius E K and Rissanen K 2001 *Chem. Lett.* **11** 1176
19. Gutsche C D and Iqbal M 1989 O*rg. Syn.* **68** 234
20. Casnati A, Fisher C, Guardigli M, Isernia A, Manet I, Sabbatini N and Ungaro R 1995 *J. Chem. Soc., Perkin Trans.* **2** 395
21. Ali A and Rao C P 2005 *Indian J. Chem.* **B44** 549
22. Arduini A, Ghidini E. Pochini A, Ungaro R, Andreetti G D, Calestani G and Ugozzoli F 1988 *J. Incl. Phenom.* **6** 119
23. Hanna T A, Liu L, Zakharov L N, Rheingold A L, Watson W H and Gutsche C D 2002 *Terahedron* **58** 9751
24. Andreetti A D, Pochini A and Ungaro R 1983 *J. Chem. Soc., Perkin Trans.* **2** 1773