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Heterocalixarenes. Part 2. Calix[*m*]uracil[*n*]benzimidazol-2(1*H*)-one[3] arenes: Synthesis and Binding Characteristics ⋆

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Abstract. The reactions of uracil/benzimidazol-2(1*H*)-one with 1,3-bis(bromomethyl)benzene provide respectively 1 3-bis[(3-bromomethylbenzene)methyl]uracil/benzimidazol-2(1*H*)-one which on subsequent cyclization with 1,3-bis[(uracil-1-yl/benzimidazol-2(1*H*)-one-1-yl)methyl]benzene derivatives provide respectively calix[*m*]uracil[*n*]benzimidazoI-2(1*H*)-one[3]arenes [*m* =3, *n* = 0 (**9**); *m* = 2, *n* = 1 (**10**); *m* = 1, *n* = 2 (**11**) and *m* = 0, *n* = 3 (**12**)]. The heterocalixarenes **9–12**, both in liquid–liquid and solid–liquid extraction experiments, selectively extract ammonium picrates over the similarly sized K^+ picrate. The selectivity is much more pronounced in the case of solid-liquid extractions. Both in L-L and S-L extractions, **10** exhibits the highest order of *t*-$BuNH_3^+/K^+$ selectivity.

Key words: heterocalix[6]arenes, uracil, benzimidazole-2(1*H*)-one, *t*-butylammonium picrate extractions (S-L; L-L)

1. Introduction and Design

The molecular recognition of biological amines and amino acids by synthetic receptors has helped us to understand their mode of participation in biological reactions [2]. 18-Crown-6 and its derivatives [3] show reasonable binding towards monoalkyl-/aryl-ammonium cations through three $NH_{amine}\cdots O_{CE}$ H-bonding interactions but the participation of additional ether units leads to a strong binding character for K^+ and other similar sized cations. As a result, poor ammonium/K^+ selectivities are observed. In recent years, the calixarenes [4], due to their preorganisation have shown remarkable potential in development of selective binding receptors. We envisaged that a calixarene possessing only three binding sites organised at trigonal positions, which is essential for binding with RNH_3^+ cations, would provide reasonable RNH_3^+/K^+ selectivities. Since the urea oxygens [5] are the most electron rich amongst hard oxygen bases, investigations of heterocalix[6]arenes (Model I), possessing three alternate cyclic urea and three arene rings were planned.

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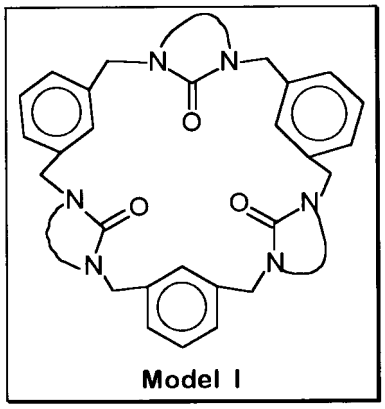


Model 1.

In the present investigations, four heterocalix[6]arenes **9–12** possessing uracil or benzimidazole-2(1*H*)-one and their combinations as the cyclic urea units placed at alternate positions have been synthesized and their binding characteristics towards methylammonium, *t*-butylammonium and K^+ picrates have been determined.

2. Experimental

The melting points were determined in open capillaries and are uncorrected. Thin layer chromatography was used for monitoring the progress of the reaction and for comparison with authentic samples. For this purpose, microslides were coated with Silica Gel-G or Silica Gel HF254 and developed in an iodine chamber or under a UVGL-15 mineral light 254 lamp (in the case of HF-254 silica gel coated plates). The chromatographic purification of reaction products was performed on silica gel (6O–120 mesh) packed columns with hexane, ethyl acetate, chloroform and their mixtures as eluent.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200E instrument using tetramethylsilane as internal standard in $CDCl_3$. Chemical shifts are expressed as δ downfield from TMS; J values are in Hz. IR spectra were recorded on a Shimadzu FTIR-1810 instrument using KBr (solid) as the medium. ES (electrospray) and EI mass spectra were recorded on a Micromass Quattro II triple quadrupole instrument (at Central Drug Research Institute, Lucknow) and Shimadzu GCMS-QP-2000 mass spectrometers, respectively. The elemental analysis were performed on a Perkin Elmer - 2400 instrument (at the Regional Sophisticated Instrumentation Center, Chandigarh).

Uracil and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) were procured from Loba, India and Lancaster, England, respectively. l,3-Bis(bromomethyl)benzene (**2**) [6] and *N*-propen-2-ylbenzimidazol-2(1*H*)-one (**3**) [7] were prepared according to the reported procedures.

2.1. SYNTHESIS OF DIBROMIDES **3**, **5** AND **6**: A GENERAL PROCEDURE

To a suspension of NaH (0.9 g, 0.022 mol) (pre-washed with dry hexane) in DMF (50 mL) was added uracil (**1**) (1.12 g, 0.01 mol), followed by stirring at room temperature for 30 minutes. 1,3-Bis(bromomethyl)benzene (**2**) (21.5 g, 0.08 mol) and tetramethylammonium hydrogen sulphate (TBA HSO_4 (50 mg) dissolved in 100 mL of DMF were added at once and the reaction mixture was stirred for 24 hours at room temperature. After completion of the reaction, acetic acid (0.5 mL) was added and the solvents were removed under vacuum. The residue was dissolved in dichloromethane and filtered through fluted filter paper. The solvent was distilled off and the residue was column chromatographed on Silica Gel (60–120 mesh) using hexane : ethyl acetate (9 : 1) as eluent to get pure **3**. Similarly the reaction of benzimidazol-2(1*H*)-one (**4**) with 1,3-bis(bromomethyl)benzene provided the dibromides **5** and **6**.

1,3-Bis[(3-bromomethylbenzene)methyl]uracil **(3)**. (42%); (24 h), mp 85–87 °C (MeOH); MS *m/z* 476, 478, 480 (M^+); ^{1}H NMR ($CDCl_3$): δ 4.46(4H, s, 2 × CH_2Br), 4.90(2H, s, NCH_2), 5.12(2H, s, NCH_2), 5.77(1H, d, J = 7.8Hz, U5-H), 7.11–7.49(9H, m, U6-H and 8 × ArH); ^{13}C NMR ($CDCl_3$) normal(DEPT-135): δ 32.72(−ve, CH_2Br), 33.34 (−ve, CH_2Br), 43.99(−ve, NCH_2), 51.96(−ve, NCH_2), 102.06(+ve, U5-H), 127.69(+ve, ArCH), 128.30(+ve, ArCH), 128.78(+ve, ArCH), 128.90(+ve, ArCH), 129.00(+ve, ArCH), 129.33(+ve, ArCH), 129.46(+ve, ArCH), 135.85(absent, ArC), 137.16(absent, ArC), 137.77(absent, ArC), 138.63(absent, ArC), 141.88(+ve, U6-H), 151.51(absent, C=O), 162.61 (absent, C=O) IR(KBr) ν_{max} (cm^{-1}): 1650–1690(m, C=O).

1,3-Bis[(3-bromomethylbenzene)methyl]benzimidazol-2(1H)-one (**5**). (62%); (24 h), mp 102 °C (MeOH); MS *m/z* 498, 500, 502 (M^+); ^{1}H NMR ($CDCl_3$): δ 4.44(4H, s, 2 × CH_2Br), 5.10(4H, s, 2 × NCH_2), 6.83–6.94(4H, m, ArH), 7.22–7.36(8H, m, ArH); ^{13}C NMR ($CDCl_3$) normal(DEPT-135): δ 32.83(−ve, CH_2Br), 44.76(−ve, NCH_2), 108.27(+ve, ArCH), 121.61(+ve, ArCH), 1 26.82(+ve, ArCH), 127.46(+ve, ArCH), 128.10(+ve, ArCH), 128.54(absent, ArC), 129.30(+ve, ArCH), 136.99(absent, ArC), 138.43(absent, ArC), 154.34(absent, C=O); IR(KBr) ν_{max} (cm^{-1}): 1688 (s, C=O).

1,3-Bis[(3-(3-bromomethylbenzyl)benzimidazol-2(1H)-one-1-yl)methyl]benzene (**6**). (12%); (24 h), thick liquid, MS *m/z* 734, 736, 738(M^+); ^{1}H NMR ($CDCl_3$): δ 4.44(4H, 5, 2 × CH_2Br), 5.09(8H, s, 4 × NCH_2), 6.70–6.93(8H, m, ArH), 7.23–7.36(12H, m, ArH); ^{13}C NMR ($CDCl_3$) normal(DEPT-135): δ 32.54(−ve, CH_2Br), 44.23(−ve, NCH_2), 107. 67 (+ve, ArCH), 107.82(+ve, ArCH), 120.98(+ve, ArCH), 126.32(+ve, ArCH),126.93(+ve, ArCH), 127.59(+ve, ArCH), 127.98(+ve, ArCH), 128.62(+ve, ArCH), 128.75(+ve, ArCH), 128.90(absent, ArC), 136.48(absent, C), 136.56(absent, C), 137.86(absent, C), 153.78(absent, C=O): IR(KBr) ν_{max} (cm^{-1}):1645(s, C=O), 1670–1710(m, C=O).

1,3-Bis(1-uracilylmethyl)benzene (**7**):. A solution of 2,4-bis(trimethylsilyloxy) pyrimidine [8] (1.96 g, 001 mol), **2** (1.32 g, 0.005 mol) and I_2 (20 mg) in 1,2-dichloroethane (20 mL) was heated to reflux and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to 5 °C and methanol (15 ml) was added. After a few minutes the separated solid was filtered and recrystallized from methanol to obtain pure **7**. (60%); (48 h), mp 268 °C (AcOH+H_2Q); MS *m/z* 326(M^+); ^{1}H NMR (200MHz, $CDCl_3$+TFA): δ 5.18 (4H, 5, 2 × NCH_2), 6.21(2 H, d, J = 7.8Hz, U5-H), 7.23–7.43 (4H, m, Ar-H), 7.52 (2H, d, J = 7.8 Hz, U6-H); ^{13}C NMR (normal/DEPT-135) (50MHz, $CDCl_3$ + DMSO-d_6): δ 49.68(−ve, NCH_2), 101.28 (+ve, C5-H). 126.49 (+ve, ArCH), 128.42 (+ve, ArCH), 135.82 (absent, C),140.05 (+ve, ArCH), 143.60 (+ve, C6-H), 150.34 (absent, C), 163.18 (absent, C) IR ν_{max}/cm^{-1} (KBr): 3200(NH). 1700 (C=O), 1658(C=O); (found: C 58.55, H 4.02, N 17.57; $C_{16}H_{14}O_4N_4$ requires C 58.90, H 4.29, N 17.18).

1,3-Bis[(benzimidazol-2(1H)-one-1-yl)methyl]benzene (**8**). A suspension of 1-(propen-2-yl)benzimidazol-2(1H)-one (1.74 g, 0.01 mol) in acetonitrile (100 mL) containing 1,3-bis(bromomethyl)benzene (**2**) (5.28 g, 0.02 mol), K_2CO_3 (5 g) and TBA HSO_4 (50 mg) was heated to reflux and the progress of the reaction was monitored by TLC. After completion of the reaction, suspended solid was filtered off and was washed with acetonitrile. The filtrate and washings were combined, the solvent was distilled off and the residue was dissolved in ethanol and sulphuric acid (50%, 10 mL) was then added dropwise with stirring. After 4 h the crude product was filtered off and washed with cold water and recrystallized from acetic acid, (80%), mp 308 °C, MS *m/z* 370(M^+); ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.11(4H, s, NCH_2), 6.92–7.34(12H, m, 12 × ArH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 45.20(−ve, NCH_2), 109.99(+ve, ArCH), 112.03(+ve, ArCH), 123. 85(+ve, ArCH), 124.34(+ve, ArCH), 126.03(+ve, ArCH), 127.24(absent, ArC), 127.44(+ve, ArCH), 129.09(absent, ArC), 130.26(+ve, ArCH), 135.79(absent, ArC), 155.65(absent, C=O); IR(KBr) ν_{max} (cm^{-1}): 1690–1720(m, C=O). (Found: C, 71.58; H, 5.12; N, 14.82%. $C_{22}H_{22}N_4O_2$ requires C, 71.35; H, 4.86; N, 15.14%).

2.2. SYNTHESIS OF HETEROCALIX[6]ARENES **9–12**: GENERAL SYNTHESIS

A suspension of **7** (3.26 g, 0.01 mol) in acetonitrite (600 mL) containing dibromide **3** (4.78 g, 0.01 mol), K_2Co_3 (15 g) and TBA HSO_4 (100 mg) was heated to reflux and the progress of the reaction was monitored by TLC. After completion of the reaction, suspended solid was filtered off and washed with acetonitrile. The filtrate and washings were combined, the solvent was distilled off and the residue was column chromatographed on silica gel (60–120 mesh) using ethyl acetate : chloroform (1 : 9) as eluent to isolate calix[3]uracil[3]arene (**9**). Similarly, the reactions of **7** with dibromide **5**; and **8** with dibromides **3** and **5** provide the heterocalix[6]arenes **10**, **11** and **12**, respectively.

Calix[3]uracil[3]arene (**9**). (60%); (36 h), mp 210–20 °C; ES MS *m/z* 643 (M^++H); ^{1}H NMR ($CDCl_3$: δ 4.85(2H, s, NCH_2), 4.87(4H, s, NCH_2), 5.10(2H, s, NCH_2), 5.12(2H, s, NCH_2). 5.15(2H, s, NCH_2), 5.73(1H, d, J = 7.8Hz, U5-H), 5.74(1H, d, J = 7.8Hz, U5-H), 5.75(1H, d, J = 7.8Hz, U5-H), 7.01–7.44(15H, m, ArCH and C6-H); ^{13}C NMR ($CDCl_3$) normal(DEPT-135): δ. 43.85(−ve, NCH_2), 58.00(−ve, NCH_2), 101.71(+ve, C5-H), 101.95(+ve, C5-H), 126.11(+ve, ArCH), 126.50(+ve, ArCH), 126.96(+ve, ArCH), 127.29(+ve, ArCH), 127.82(+ve, ArCH), 128.33(+ve, ArCH), 128.59(+ve, ArCH), 128.99(+ve, ArCH), 129.55(+ve, ArCH), 135.31(absent, ArC), 136.22(absent, ArC), 136.63(absent, ArC), 137.53(absent, ArC), 141.93(+ve, C6-H), 151.49(absent, C=O), 162.48(absent, C=O) ; IR (KBr) ν_{max} (cm^{-1}): 1659(C=O). (Found: C, 66.9; H, 4.7; N, 13.4% $C_{36}H_{30}N_6O_6$ requires C, 67.29; H, 4.67; N, 13.08%).

Calix[2]uracil[1]benzimidazol-2(1H)-one[3]arene (**10**). (42%); (36 h), mp 1 68 °C (d); ES MS *m/z* 665 (M^++H); ^{1}H NMR ($CDCl_3$): δ 4.85(4H, s, 2 × NCH_2), 5.07(4H, s, 2 × NCH_2). 5.09(4H, s, 2 × NCH_2), 5.70(+ve, U5-H), 6.85–7.56(18H, m, 18 × ArCH); ^{13}C NMR ($CDCl_3$) normal(DEPT-135): δ 44.06(−ve, NCH_2), 44.66(−ve, NCH_2), 52.00(−ve, NCH_2), 101.94(+ve, U5-H), 108.26(+ve, ArCH), 121.28(+ve, ArCH), 125.07(+ve, ArCH), 126.39(+ve, ArCH), 127.36(+ve, ArCH), 127.62(+ve, ArCH), 127.94(+ve, ArCH), 128.37(+ve, ArCH), 128.85(+ve, ArCH), 129.06(absent, ArC), 129.70(+ve, ArCH), 136.34(absent, ArC), 136.77(absent, ArC), 137.11(absent, ArC), 142.02(+ve, U6-H), 151.49(absent, C=O), 154.32(absent, C=O), 162.61(absent, C=O); IR(kBr) ν_{max} (cm^{-1}): 1650(s, C=O), 1695(s, C=O). (Found: C, 70.1; H, 4.7; N, 12.7%. $C_{39}H_{32}N_6O_5$ requires C, 70.48; H, 4.82; N, 12.65%).

Calix[1]uracil[2]benzimidazol-2(1H)-one[3]arene (**11**). (42%); (36 h), mp 165-72 °C; ES MS *m/z* 687(M^++H); ^{1}H NMR ($CDCl_3$): δ 4.70(2H, s, NCH_2), 4.94(2H, s, NCH_2), 4.97(2H, s, NCH_2), 5.01(2H, s, NCH_2), 5.06(2H, s, NCH_2), 5.10(2H, s, NCH_2), 5.65(1H, d, J = 8.0Hz, U5-H), 6.56–7.34(21H, m, 20 × ArCH and 1 × U6-H); ^{13}C NMR ($CDCl_3$) normal(DEPT-135): δ 43.57(−ve NCH_2), 44.14(−ve, NCH_2) 44.39(−ve, NCH_2), 44.66(−ve, NCH_2), 51.77(−ve, NCH_2), 101.64(+ve, U5-H), 107.97(+ve, ArCH), 108.19(+ve, ArCH), 121.10(+ve, ArCH), 121.20(+ve, ArCH), 121.44(+ve, ArCH), 125.45(+ve, ArCH), 125.60(+ve, ArCH), 125.83(+ve, ArCH), 125.93(+ve, ArCH), 126.30(+ve, ArCH), 126.49(+ve, ArCH), 126.58(+ve, ArCH), 127.17(+ve, ArCH), 127.87(absent, ArCH), 128.21(absent, ArCH), 128.69(+ve, ArCH), 128.82(+ve, ArCH), 128.94(+ve, ArCH), 129.05(+ve, ArCH), 129.33(+ve, ArCH), 135.80(absent, ArCH), 136.28(absent, ArCH), 136.74(absent, ArCH), 137.10(absent, ArCH), 141.70(+ve, U6-H), 151.35(absent, C=O), 154.39(absent, C=O), 154.49(absent, C=O), 162.33(absent, C=O); IR(KBr) ν_{max} (cm^{-1}): 1665(s, C=O), 1708(s, C=O). (Found: C, 73.8; H, 5.3; N, 12.6%. $C_{42}H_{34}N_6O_4$ requires C, 73.47; H, 4.96; N, 12.24%).

Calix[3]benzimidazol-2(1H)-one[3]arene (**12**). (65%); (36 h), mp 152–56 °C; ES MS *m/z* 709 (M^++H): ^{1}H NMR ($CDCl_3$): δ 4.96(12H, s, 6 × NCH_2), 6.58–6.63(6H, m, ArCH), 6.77–6.84(6H, m, ArCH), 7.17–7.33(12H, m, ArCH); ^{13}C NMR ($CDCl_3$) normal(DEPT-135): δ 44.47(−ve, NCH_2), 108.22(+ve, ArCH), 121.28(+ve, ArCH), 124.83(+ve, ArCH), 126.11(+ve, ArCH), 128.93(+ve, ArCH), 129.09(absent, ArC), 136.80(absent, ArC), 154.50(absent, C=O); IR(KBr) ν_{max} (cm^{-1}): 1695(s, C=O). (Found: C, 76.5; H, 5.5; N, 11.5%. $C_{45}H_{36}N_6O_3$ requires C, 76.27, H, 5.08; N, 11.86%).

2.3. EXTRACTION MEASUREMENTS

2.3.1. (a) *Liquid–liquid extractions [9]*

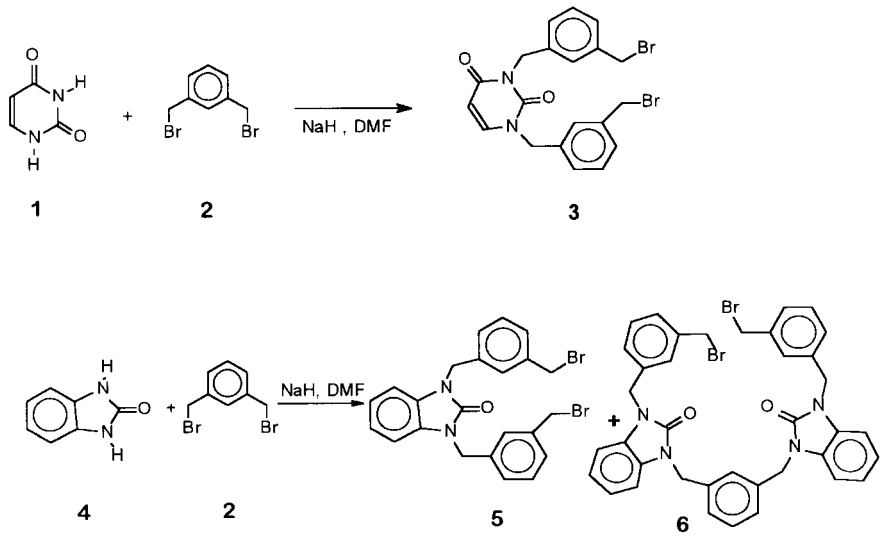
An aqueous solution (2 mL) of metal picrates (0.01 mol dm^{-3}), prepared in deionised double distilled water, and a chloroform solution (2 mL) of heterocalix[6]arenes (0.01 mol dm^{-3}), were shaken in a cylindrical tube closed with a septum, for 5 minutes and kept at 27 ± 1 °C for 34 h. An aliquot of the chloroform layer (1 mL) was withdrawn with a syringe and diluted with acetonitrile to 10 mL. Its UV absorption was measured against $CHCl_3$—CH_3CN (1 : 9) solution at 374 nm. Extraction of picrate has been calculated as the percentages of picrate extracted in the chloroform layer and the values reported here are the mean of three independent measurements which were within ±0.02% error.

2.3.2. (b) *Solid–liquid extractions [10]*

The finely ground picrates were added to 0.5 mL of the heterocalix[6]arene (0.01 mol dm^{-3}) solutions and the mixtures were stirred for an extended period of time and kept at 27 ± 1 °C for 2–3 hours. The mixtures were then centrifuged and filtered to remove all solid material. The picrates extracted were determined by UV spectrometry as described above. To provide the necessary reference datum, the same determination was carried out with a system not containing the heterocalix[6]arenes and final extractions were calculated after applying the correction for extraction in blank experiments.

2.4. ENERGY MINIMIZATION STUDIES

The energy minimization studies were performed on PCMODEL software version 5.13 provided by Serena software, without any further modification. The programme uses molecular mechanics potentials and the force fields of Allinger, with extensions and modifications to handle more functional groups. These include bond stretching potentials, bond angle deformation potentials, periodic torsional barrier potentials, and non-bonding interactions for non-bonded atom pairs. It provides facilities for conformational space hunting, charge calculation and hydrogen bonding.



Scheme 1.

Table I. The PCMODEL based NH—O H-bond distances for *t*-butylammonium cation complexes with heterocalixarene **9–12**

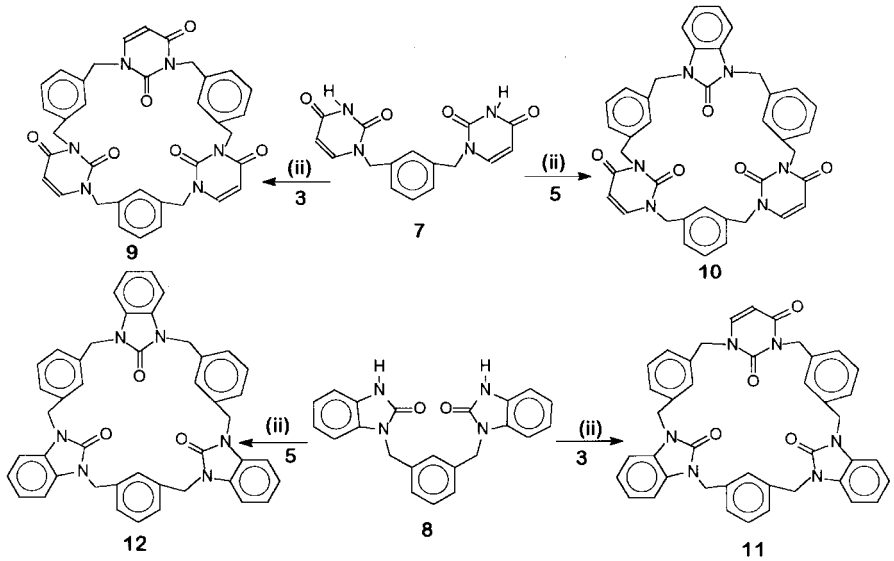
Heterocalixarene	NH—O distance (Å)	MMX energy (kJ mol^{-1}) Heterocalixarene E_1	Complex E_2	Stabilization energy $\Delta E = E_2 - E_2$ (kJ mol^{-1})
9	1.77 ± 0.02	−23.75	−55.25	−31.50
10	1.63 ± 0.05	3.57	−38.10	−41.67
11	1.75 ± 0.05	43.19	−1.15	−44.34
12	1.70 ± 0.05	69.62	19.75	−49.87

3. Results and Discussion

3.1. SYNTHESIS

The reaction of uracil (**1**) with 1,3-bis(bromomethyl)benzene in DMF containing a suspension of NaH gives dibromides **3** (42%). Similarly, reaction of benzimidazole-(1*H*)-one (**4**) with 1,3-bis(bromo-methyl)benzene provides dibromides **5** (62%) and **6** (12%) (Scheme 1).

Cyclocondensations of **7** with dibromides **3** and **5** under phase transfer catalytic conditions (K_2CO_3—CH_3CN—TBA HSO_4) provide calix[3]uracil[3]arene (**9**) (60%), and calix[2]uracil[1]benzimidazole-2(1*H*)-one[3]arene (**10**) (42%), respectively. Similarly, the reactions of **8** with **3** and **5** give calix[2]benzimidazol-2(1*H*)-one[1]uracil[3]arene (**11**) (42%), and calix[3] benzimidazol-2(1*H*)-one[3]arene (**12**) (65%), respectively (Scheme 2). Alternatively, **11** (65%) could also be synthesized by the cyclocondensation of dibromide **6**with uracil.



Scheme 2.

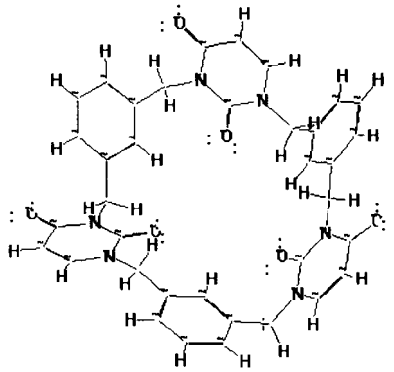


Figure 1a. Energy minimised structure of calix[3]uracil[3]arene.

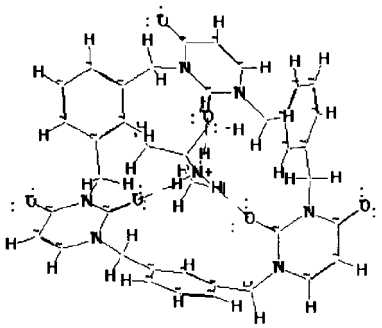
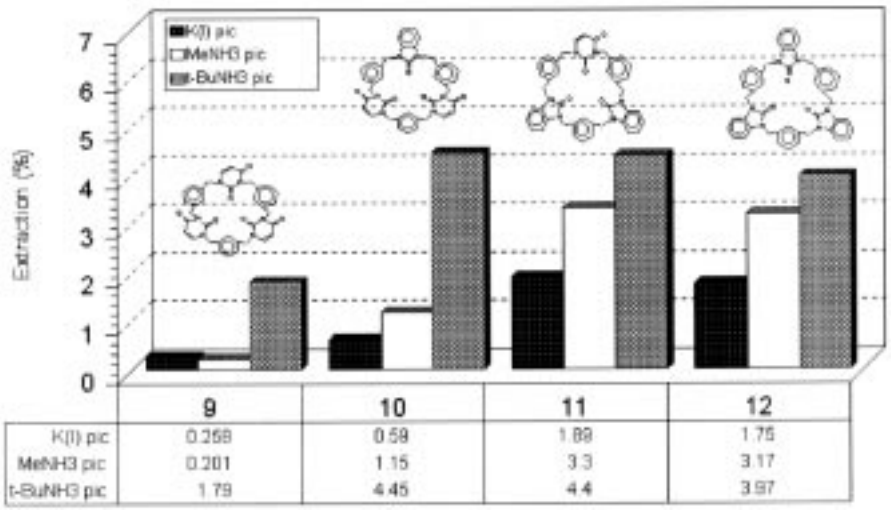
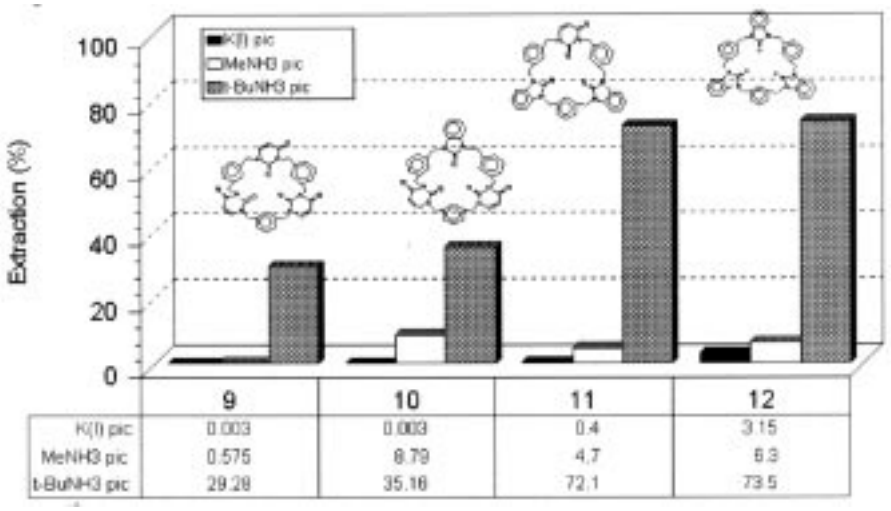


Figure 1b. Energy minimised structure of calix[3]uracil[3]arene.*t*-butylammonium cation complex.



	9	10	11	12
K(I) pic	0.258	0.59	1.89	1.75
MeNH3 pic	0.201	1.15	3.3	3.17
t-BuNH3 pic	1.79	4.45	4.4	3.97

Figure 2. Liquid–liquid extraction profile of heterocalix[6]arenes **9–12**.



	9	10	11	12
K(I) pic	0.003	0.003	0.4	3.15
MeNH3 pic	0.575	8.79	4.7	6.3
t-BuNH3 pic	29.28	35.16	72.1	73.5

Figure 3. Solid–liquid extraction profile of heterocalix[6]arenes **9–12**.

The ^{1}H NMR spectrum of calix[3]benzimidazol-2(1*H*)-one[3]arene (**12**) exhibits one singlet due to six NCH_2 units and multiplets due to ArH. However, multiple signals are observed in the uracil based calixarenes **9–11**, due to non-equivalence of the N-1 and N-3 nitrogens. The calix[3]uracil[3]arene (**9**) exhibits five singlets for the six NCH_2 groups and three doublets due to C-5H of three uracil units, along with multiplets of uracil C-6H and aromatic protons. Similarly, **11** exhibits six singlets and **10** exhibits singlets due to six NCH_2 units each. Therefore, the calixarenes **9–12** have quite flexible structures and the ^{1}H NMR spectra might be the average of various conformations.

3.2. ENERGY MINIMIZATION STUDIES

The energy minimizations on **9–12** show that these four heterocalixarenes and their complexes with *t*-butylammonium cation exhibit similar energy minimized structures. In a representative case, energy minimized structures of **9** and the **9.t-butylammonium cation** complex (Figure 1) show that in the parent molecule, two imide carbonyl oxygens of two heterocyclic units remain directed inward to the cavity and the third imide carbonyl group is placed outside the cavity. But on complexation, all the three imide carbonyl oxygens are directed inward to the cavity and form H-bonds with three hydrogens of the RNH_3^+ group. The NH$\cdots$O distances are nearly equal in the range 1.60–1.80 Å [11]. In all the cases, the complexes are stabilized by -30 to 50 kJ mol^{-1} in comparison with their parent heterocalixarene molecule (Table I) Therefore, the energy minimization studies support the contention that model I, through H-bonds between three imide carbonyl oxygens and ammonium H, would form stable complexes with alkylammonium salts.

3.3. BINDING CHARACTERISTICS

In order to evaluate the selective binding characteristics of calixarenes **9–12**, the liquid–liquid (water $CDCl_3$) and solid–liquid ($CDCl_3$) extractions of K^+, $CH_3NH_3^+$ and *t*-butylNH_3^+ picrates nave been performed. The heterocalixarenes **9–12** show a similar order of binding preferences: *t*-butylammonium > methylammonium > K^+ picrate (Figures 2 and 3) but with an increase in the number of benzimidazole-2(1*H*)-one units from 1–3, the selectivity towards *t*-butylammonium picrate decreases (Figures 4 and 5). In solid–liquid extractions, due to the lack of water–cation interactions, the much higher order of extraction and also *t*-$BuNH_3^+/K^+$ selectivity is observed.

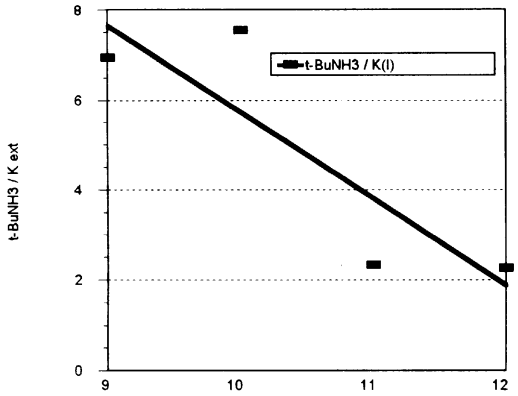


Figure 4. In liquid–liquid extractions, *t*-butylammonium and methylammonium over K^+ selectivity in **9–12**.

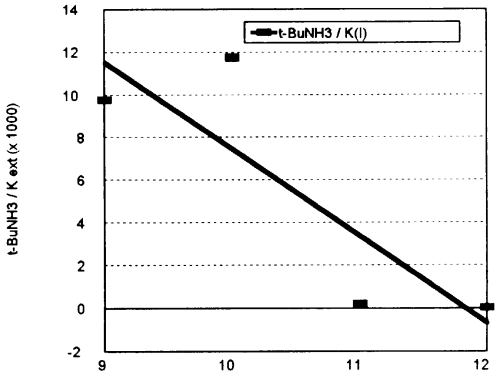


Figure 5. In solid–liquid extractions, *t*-butylammonium and methylammonium over K^+ selectivity in **9–12**.

In liquid–liquid extractions, **9** extracts *t*-$BuNH_3^+$ picrate (1.79%) nearly seven times more effectively than K^+ picrate and in the case of **10**, both the extraction of *t*-$BuNH_3^+$ (4.45%) and its selectivity over K^+ (eight times) increases. However, an increase in the number of benzimidazol-2(1*H*)-one units in **11** and **12**, further increases the extraction of K^+ but does not affect the extraction of *t*-$BuNH_3^+$ picrate and thus results in a lowering of selectivity. In solid–liquid extractions, K^+ is extracted only marginally but $MeNH_3^+$ and *t*-$BuNH_3^+$ picrates are extracted with higher efficiency. The receptor **10** extracts *t*-$BuNH_3^+$ picrate nearly 11 500 times greater than K^+ picrate. However, as observed in the case of the liquid–liquid extractions, the increase in the number of benzimidazol-2(1*H*)-one units increases the extraction of K^+ picrate more efficiently than that of *t*-$BuNH_3^+$ picrate and results in a lower *t*$BuNH_3^+/K^+$ selectivity.

The comparison of these results with those reported earlier for dicyclohexyl 18-C-6 (**13**) and 2,3-naphtho 18-C-6 (**14**) shows that **13** and **14** extract K^+ picrate preferentially over *t*-$BuNH_3^+$ picrate by 16 and 10 times, respectively, while the present calixarenes **9–12** (especially **10**) extracts *t*-$BuNH_3^+$ picrate nearly eight times (in L-L extractions) and 11 500 times (in S-L extractions) more efficiently than K^+ picrate. Thus, **9–12** are efficient and selective receptors for RNH_3^+ cations over the similar sized K^+ cation.

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