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Bis(imidazolium)−Calix[4]arene Receptors for Anion Binding†

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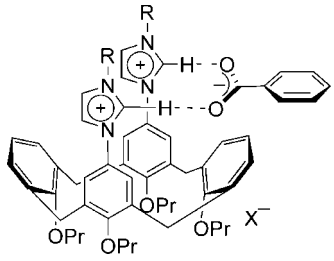

Efficient access to the bis(imidazolyl)calixarene **2** and dicationic bis(imidazolium) salts **1a**,**b**·**2X** directly bonded to the upper rim of calixarene structure has been reported. Anion binding properties of the new receptors were studied by ^{1}H NMR spectroscopic methods. Bis(*N*-butylimidazolium) dication **1a** exhibited the best recognition properties toward carboxylate anions with a 1:1 receptor−anion binding stoichiometry, whereas the presence of a bulky group such as isopropyl (**1b**) increased the difficulty of both imidazolium moieties to be able to support the association with the same single anion.

Anions play a number of fundamental roles in biological and chemical processes and the development of selective anion receptors is an area of current importance. Accordingly, anion recognition chemistry includes current developments in anion-template synthesis and selective artificial anion receptors, especially positively charged systems.[1,2] Imidazolium groups provide both a positive charge and relatively acidic CH group with which to bind anionic species. The use of imidazolium salts as a recognition element for anions has already been demonstrated, from the first example in the solid state[3] to the observed template assembly of mechanically interlocked structures.[2b] Hence such moieties included in dicationic heterophanes have been employed for anion recognition using the strong $(C-H)^+\cdots X^-$ hydrogen bonding between imidazolium units and halide anions[1,4] and oxoanions.[5] Furthermore, imidazolium salts have been used in ditopic and tripodal benzene anion receptors[2f,6] and have been attached to the upper rim of a resorciarene, acting as a basic skeleton of an anion receptor, using flexible linker groups showing good affinity for inorganic anions,[7a] carboxylates,[7a] and dicarboxylates.[7b]

In parallel, calixarenes are particularly attractive scaffolds for receptor development, the macrocyclic core being available in a variety of sizes, easily preorganized into a number of topographies and readily selectively functionalized for the opposite introduction of ligands.[8] Related calixpyrroles show affinity for inorganic anions[9] as well as functionalized calixarenes in the upper or lower rim.[8b,10] Remarkably, only one example, reported by Schatz and co-workers,[11] includes imidazolium moieties incorporated in the upper rim of calyx[4]arene using a methylene linker. Di- and tetracationic systems have been studied as anion receptors for spherical (Cl^- and Br^-) or tetrahedral ($H_2PO_4^-$ and HSO_4^-) inorganic anions[11a] and citrate.[11b]

As part of our ongoing research into imidazolium-based frameworks,[1,12] we herein report the synthesis of the original bis(*N*-imidazolyl)calyx[4]arene **2** system, with two imidazole units directly bonded to the upper rim of the calixarene structure, together with its quaternization that provided bis(imidazolium)

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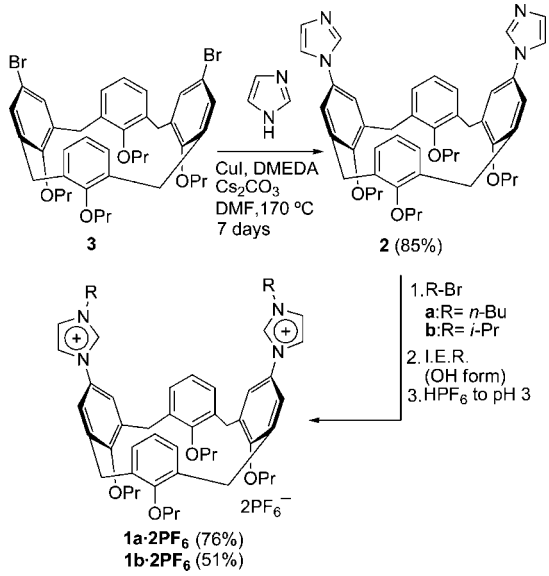
SCHEME 1



cations **1a** and **1b**. Anion binding properties of the new receptors were studied by ^{1}H NMR spectroscopic methods.

To prepare 5,17-bis(imidazolyl)calixarene **2** we considered a condensation between 5,17-dibromo-25,26,27,28-tetrapropoxycalix[4]arene **3** and imidazole. To carry out the N-arylation of imidazole, the copper-catalyzed Ullmann-type reaction is the most efficient method. Most couplings of imidazoles use aryl iodides as the electrophilic coupling partner and only a few examples with aryl bromides are reported.[13] Furthermore, the difficulty of synthesizing our target compound **2** was increased since it was necessary to perform due to a double coupling in a preorganized system like calyx[4]arene in cone conformation. Thus, we considered applying Cu-catalyzed sterically hindered *N*-arylimidazole conditions,[13a] and the double condensation was achieved by using 20 mol % of air-stable CuI in combination with 80 mol % of *N*,*N*-dimethylethylenediamine (DMEDA) as ligand, 1 M in DMF, together with Cs_2CO_3 as the base in a sealed tube at 170 °C during 48 h. However, the bis(imidazolyl)calixarene **2** was obtained in a low yield (11%).

Several reaction conditions were investigated and finally, when equimolecular amounts of CuI and DMEDA (50 mol % for each imidazole coupling) and dibromocalix[4]arene **3** were used for 7 days, the yield was increased to 89% (see Scheme 1).

In the next step the bis(imidazolium)calyx[4]arene dications **1a** and **1b** as dibromide salts were prepared[12] by quaternization of imidazole units of the calixarene **2** by using 1-bromobutane or 2-bromopropane. Thereafter, counterion exchange was performed according to our standard protocol[4] to obtain **1a·2PF$_6$** and **1b·2PF$_6$** salts.

Anion binding properties of the new receptors were studied by ^{1}H NMR spectroscopic methods at 300 MHz. Aliquots of tetrabutylammonium salts of putative anionic guests were added to a solution of compounds **1a·2PF$_6$** (ca. 6 mM) or **1b·2PF$_6$** (ca. 3 mM) in CD_3CN or DMSO-d_6. Both hosts exhibited downfield shifts of the C(2)H signal of the imidazolium moieties upon addition of the anions. No significant shifts of the other proton signals of the receptor molecules could be observed, indicating that the anions were bound by $(C-H)^+\cdots X^-$ hydrogen bonding. Monitoring the imidazolium proton resonance produced titration curves and Job plots (see the Supporting Information), which, after WinEQNMR computer program[14] analysis of the titration gave the binding isotherms and stability constant values summarized in Table 1.

TABLE 1. Anion Binding Properties of Dication 1a and 1b (Anion Complexes Based on ^{1}H NMR Experiments (300 MHz))[a]

anion	K_a (M^{-1})	$\Delta G°$ (KJ)	K_a (M^{-1})	$\Delta G°$ (KJ)
1a·2PF$_6$	CD_3CN		DMSO-d_6	
Cl^-	222	14.2	$K_1 = 1801$; $K_2 = 48$	19.7[b]
Br^-	215	14.1	*c*	
CN^-	157	13.3	*c*	
$H_2PO_4^-$	*d*		$K_1 = 2446$; $K_2 = 51$	20.5[b]
$CH_3CO_2^-$	232[e]	14.3	*f*	
$C_6H_5CO_2^-$	404	15.8	$K_1 = 5804$; $K_2 = 22$	22.8[b]
malonate^{2-}	1142[e]	18.5		
1b·2PF$_6$	CD_3CN		DMSO-d_6[g]	
Cl^-	598	16.8	*c*	
Br^-	$K_1 = 1824$; $K_2 = 88$	19.7[b]	*c*	
CN^-	380	15.5	*c*	
$H_2PO_4^-$	*d*		$K_1 = 58$; $K_2 = 185$	10.1[b]
$CH_3CO_2^-$	$K_1 = 4193$;[e] $K_2 = 286$	21.9[b]	$K_1 = 1119$; $K_2 = 100$	18.5[b]
$C_6H_5CO_2^-$	$K_1 = 9374$;[e] $K_2 = 429$	24.1[b]	$K_1 = 121$; $K_2 = 64$	11.9[b]
malonate^{2-}	642	17.0	$K_1 = 1003$; $K_2 = 120$	18.2[b]

[a] At 298 K. Association constant estimated errors ≤10%. [b] Calculated from the K_1. [c] When $\Delta\delta$ < 0.1 ppm, after addition of a large excess of the anion, data were not processed. [d] Precipitation occurred during tritiation. [e] Estimated error ≤20%. [f] A mixture of 1:1 and 1:2 binding stoichiometries was observed. [g] DMSO-d_6:CD_3CN (9:1).

Initially, we examined anion binding properties of 5,17-bis(3-butyl-1-imidazolium)-25,26,27,28-tetrapropoxycalix[4]arene dication **1a** in CD_3CN (see Table 1 and Figure 1) and Job plot analysis indicated a 1:1 binding stoichiometry for halide anions (Cl^- and Br^-) and CN^- as well as carboxylates such as acetate or benzoate (see the Supporting Information). Association constants were moderate for inorganic anions ($Cl^- \approx Br^- > CN^-$) despite the significant deshielding of the C(2)H signal of the imidazolium moieties after addition of 1 equiv of corresponding TBA salt (see Figure 1). Affinity increased slightly toward the carboxylates ($C_6H_5CO_2^- > CH_3CO_2^-$) and downfield shifts greater than 1 ppm were observed probably due to a strong $(C-H)^+\cdots RCO_2^-$ hydrogen bonding (see Figure 1).

Remarkably, C(4)H and C(5)H of the imidazolium units[15] gave separate signals when interaction with the anion was established (see Figure 2). Thus, upfield shift values of about 0.15 ppm were observed for C(5)H with respect to **1a·2PF$_6$**, while C(4)H remained unchanged. Moreover, the deshielding of the aromatic doublet of the C(10′)H (ca. 0.15 ppm) in the neighboring benzene ring (see Figure 2) suggested that with the anion coordination the calixarene unit adopts a pinched cone conformation with the substituted rings parallel.[16] Both pertur-

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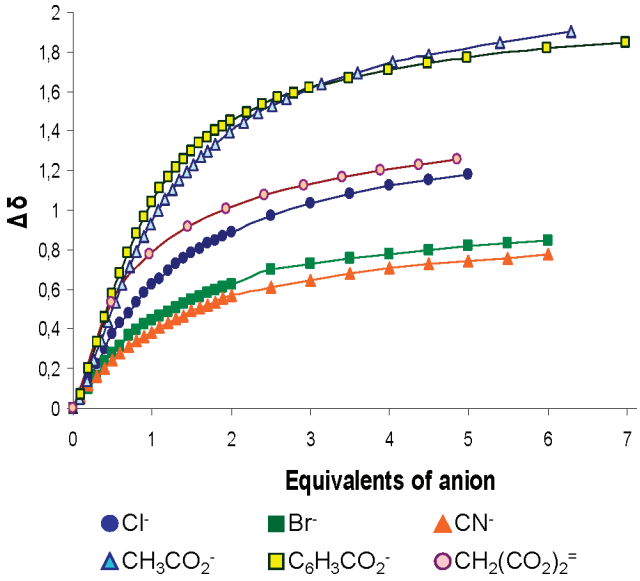

FIGURE 1. ^{1}H NMR titration curves of the receptor **1a·2PF$_6$** (initial host concentration ca. 5−6 mM in CD_3CN, 300 MHz) with corresponding TBA salts. $\Delta\delta$ is the shift difference in ppm of the imidazolium C(2)H proton.

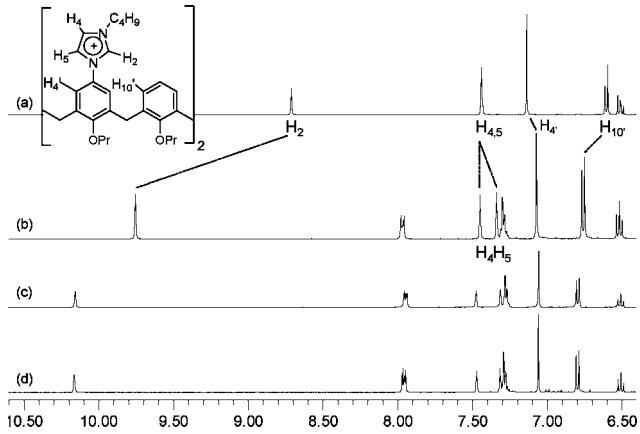

FIGURE 2. Observed perturbations in the aromatic region of the ^{1}H NMR (400 MHz) of (a) compound **1a·2PF$_6$** in CD_3CN at 298 K upon addition of (b) 1 equiv or (c) 2 equiv of TBA·$C_6H_5CO_2$, compared with (d) **1a·2C$_6$H$_5$CO$_2$** (obtained by counterion exchange).[4]

bations were present in all titrations in CD_3CN upon addition of 1 equiv of TBA·anion, with similar values for all anions recognized. Presumably, the equilibrium was established between the single anion and both imidazolium moieties and the calixarene conformation favored the binding in a perched position above the cavity.

On the other hand, addition of TBA−H_2PO_4 CD_3CN solution to a 4 mM CD_3CN solution of dication **1a·2PF$_6$** when carrying out standard titration led to the precipitation of the dihydrogen phosphate salt. The fact that precipitation occurred led us to infer that the interaction between the receptor and the dihydrogen phosphate anion is appreciable.[17]

One example of the dicarboxylate anion was examined, and TBA−malonate was used for tritiation (ca. 2.5 mM, 400 MHz). The stoichiometry of interaction was verified to be 1:1 through a Job Plot analysis, and a strong association constant was obtained (1142 M^{-1}).

To explore the anion binding properties in a more polar solvent, dication **1a** was examined in DMSO-d_6. The differences between the chemical shifts decreased in relation to CD_3CN (see Figure 3S) and when $\Delta\delta < 0.1$ ppm upon addition of a large excess of TBA·anion salt, the data were not processed (CN^- and Br^-). In this solvent, only C(2)H exhibited a significant downfield shift. Surprisingly, binding stoichiometry of 1:2 was obtained for all anions measured (see Table 1), and this was attributed to the solvating solvent effect[18] on imidazolium units. Thus, Cl^- and $C_6H_5CO_2^-$ showed large values for K_1 (10^3 M^{-1}) (see Table 1) together with the $H_2PO_4^-$ whose binding constants could be determined in DMSO-d_6 ($C_6H_5CO_2$ > H_2PO_4 > Cl^-). On the other hand, while C(5)H in the imidazolium moiety showed a slight shielding (ca. 0.1 ppm), there was no perturbation of the protons in the calixarene scaffold. These observations indicated that the conformation of calixarene does not change when recognition is produced and suggests that both imidazolium units act as independent binding sites for anions, with a solvent competition effect,[18] and confirm the affinity of imidazolium units toward oxoanions.

Regarding the acetate anion or malonate dianion with dication **1a**, a mixture of 1:1 and 1:2 binding stoichiometries was observed. In a typical titration experiment a steady downfield shift of the imidazolium protons was observed until ca. 2 equiv, whereupon a large perturbation occurred indicative of a change in binding stoichiometry (see the Supporting Information). Unfortunately, it was not possible to determine stability constant values from such titration isotherm data. Moreover, the C(2)H signal of the imidazolium moieties was developed in a broad band upon addition of the malonate, and an accurate calculation of $\Delta\delta$ became increasingly difficult.

When anion receptor properties of dication **1b** were examined in CD_3CN, a binding stoichiometry of 1:2 was obtained for almost all the anions measured (see Table 1). As expected, the volume of isopropyl groups interfered in the possible interaction between both imidazolium moieties and the anion, inside the receptor cavity. Only small anions such as Cl^- and CN^- presented 1:1 binding stoichiometry with moderated calculated association constants (598 and 380 M^{-1}, respectively), together with malonate (642 M^{-1}), while Br^-, $CH_3CO_2^-$, and $C_6H_5CO_2^-$ presented 1:2 binding stoichiometry with large K_1 (>10^3 M^{-1}) and moderate K_2 (>10^2 M^{-1}) ($C_6H_5CO_2^-$ > $CH_3CO_2^-$ > Br^-). Remarkably, when the 1:1 complex was established the perturbations in the chemical shift of C(5)H ($\Delta\delta \approx -0.1$ ppm) and C(10′)H ($\Delta\delta \approx +0.15$ ppm) were similar to that observed for the receptor **1a**, according with a pinched cone conformation in the calixarene scaffold, while in 1:2 complexes this effect was only noticeable upon addition of a large excess of TBA·anion. These observations indicated that, due to the presence of a bulky group such as isopropyl, only small anions could interact with both imidazolium moieties probably in a perched position above the cavity. However, the 1:1 binding with malonate dianion could correspond to the association with the imidazolium units in different calixarene receptors.

Finally, when titrations were carried out in DMSO-d_6-CD_3CN (9:1) exclusively with oxoanions C(2)H showed significative deshielding. As expected, binding stoichiometry of 1:2 was obtained with calculated K_1 value nearly 10^3 M^{-1} for $CH_3CO_2^-$ and malonate and lowest values for $C_6H_5CO_2^-$ and $H_2PO_4^-$ (see Table 1).

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In summary, we have synthesized the bis(*N*-imidazolyl)calyx[4]arene **2** using the copper-catalyzed Ullmann-type condensation optimized protocol for the preparation of sterically hindered *N*-arylimidazoles. Their quaternization and counterion exchange provided dicationic bis(imidazolium) salts **1a**,**b**·**2PF$_6$**, and anion binding properties of the new receptors were studied by ^{1}H NMR spectroscopic methods. Bis(*N*-butylimidazolium) dication **1a** exhibited the best recognition properties toward carboxylate anions ($C_6H_5CO_2^-$ > $CH_3CO_2^-$) together with halides (Br^- and Cl^-) in CD_3CN with a 1:1 receptor−anion binding stoichiometry probably in a perched position above the cavity, while titration in DMSO-d_6 showed 1:2 receptor−anion binding stoichiometry ($C_6H_5CO_2^-$ > $H_2PO_4^-$ > Cl^-) and confirmed the affinity of imidazolium units toward oxoanions. On the other hand, the presence of a bulky group such as isopropyl (**1b**) increased the difficulty of both imidazolium moieties to be able to support the association with the same single anion, and only small anions (Cl^- and CN^-), as well as malonate dianion, presented 1:1 binding stoichiometry in CD_3CN. Efforts are currently being directed toward the study of based imidazolium−calixarene molecular scaffolds as anion receptors and their potential application as selective sensors and supramolecular devices.

Experimental Section

5,17-Bis(1-imidazolyl)-25,26,27,28-tetrapropoxycalix[4]arene (2). An oven-dried resealable tube was back-filled with argon and charged with 5,17-dibromo-25,26,27,28-tetrapropoxycalixare[4]arene (**3**; 0.492 g, 0.656 mmol), imidazole (0.107 g, 1.572 mmol), CuI (0.127 g, 0.667 mmol), Cs_2CO_3 (0.899 g, 2.759 mmol), *N*,*N*′-dimethylethylenediamine (70 μL, 0.657 mmol), and 2 mL of dry DMF. The tube was sealed with a Teflon valve and the contents were stirred while heating at 170 °C for 7 days. The cooled reaction mixture was evaporated to dryness, and the remaining solid was dissolved in 250 mL of Cl_2CH_2 and filtered through a Celite pad. The solvent was eliminated under vacuum and solid residue was washed with acetone to afford bisimidazolyl calixarene **2** (0.42 g, 0.584 mmol, 89%) as a white solid: mp 320−322 °C. ^{1}H MNR (400 MHz, $CDCl_3$) δ 0.98 (t, 6H), 1.06 (t, 6H), 1.89−2.03 (m, 8H), 3.12 (d, 4H), 3.81 (t, 4H), 3.96 (m, 4H), 4.51 (d, 4H), 6.48 (s, 4H), 6.56 (br, 2H), 6.76 (dd, 2H), 6.85 (d, 4H), 6.94 (br, 2H), 7.38 (br, 2H). ^{13}C MNR (100.6 MHz, $CDCl_3$) δ 10.1, 10.4, 23.1, 23.3, 31.0, 76.8, 77.3, 117.7, 120.6, 122.6, 128.6, 130.1, 131.6, 135, 136.0, 155.3, 156.7. MS (EI) *m*/*z* 725 (M^+, 100%). Anal. Calcd for $C_{46}H_{52}N_4O_4\cdot 0.5C_3H_6O$ (753.99): C, 75.67; H, 7.35, N, 7.43. Found: C, 75.68; H, 7.32, N, 7.27.

General Procedure for Counterion Exchange. A solution of bisimidazolium dibromides **1a**·**2Br** or **1b**·**2Br** (0.2 mmol) in methanol (10 mL) was passed through the IRA-400 (OH form) packed column. The neutral eluates were acidified to pH 3 with a 1% v/v aqueous HPF_6 solution and concentrated to dryness. The solid residue was crystallized.

5,17-Bis(3-butyl-1-imidazolium)-25,26,27,28-tetrapropoxycalix[4]-arene Dihexafluorophospate (1a·2PF$_6$). Yield 80%; mp 226−227 °C (from methanol); ^{1}H MNR (400 MHz, CD_3CN) δ 0.96−1.07 (m, 12H), 1.35−1.44 (m, 4H), 1.84−2.06 (m, 8H), 3.31 (d, 4H), 3.83 (t, 4H), 4.03 (t, 4H), 4.18 (t, 4H), 4.54 (d, 4H), 6.54 (t, 2H), 6.64 (d, 4H), 7.11 (s, 4H), 7.40 (d, 2H), 7.44 (d, 2H), 8.70 (s, 2H); ^{13}C NMR (100.6 MHz, $CNCD_3$) δ 10.4, 10.7, 13.6, 20.0, 24.0, 31.4, 32.4, 50.7, 78.0, 122.1, 122.6, 123.4, 123.9, 129.2, 129.7, 134.5, 139.1, 134.9, 157.0, 159.1; HRMS (ESI+) *m*/*z* calcd for $C_{54}H_{70}F_6N_4O_4P$ ($M + PF_6$)$^+$ 983.5042, found 983.5033.

5,17-Bis[3-(2-propyl)-1-imidazolium]-25,26,27,28-tetrapropoxycalix[4]-arene Dihexafluorophospate (1b·2PF$_6$). Yield 53%; mp 169−170 °C (from methanol); ^{1}H MNR (400 MHz, CD_3CN) δ 1.00 (t, 6H), 1.07 (t, 6H,), 1.58 (d, 12H), 1.98−2.07 (m, 8H), 3.32 (d, 4H), 3.81 (t, 4H), 4.07 (t, 4H), 4.54 (d, 4H), 4.64 (hept, 2H), 6.49 (t, 4H), 6.59 (d, 4H), 7.21 (s, 4H), 7.50 (d, 2H), 7.54 (d, 2H), 8.79 (s, 2H); ^{13}C NMR (100.6 MHz, $CNCD_3$) δ 10.3, 10.8, 22.8, 24.0, 24.1, 31.4, 54.7, 78.0, 78.1, 122.1, 122.4, 122.7, 123.3, 129.1, 129.8, 133.8, 134.3, 139.2, 156.9, 159.2; HRMS (ESI+) *m*/*z* calcd for $C_{52}H_{66}F_6N_4O_4P$ ($M + PF_6$)$^+$ 955.4738, found: 955.4720.

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Supporting Information Available: General information, details for the synthesis of all the compounds, and anion titration data. This material is available free of charge via the Internet at http://pubs.acs.org.

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