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Anion complexation. A ditriphenylphosphonium calix[4]arene derivative as a novel receptor for anions

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Abstract—A novel anionic receptor **2** consisting of a calix[4]arene bearing two alkytriphenylphosphonium has been prepared by two different procedures. The complexation occurred at the phosphonium sites probably due to electrostatic and/or π-anion forces.

The selective extraction of anions from aqueous media by organic molecules presents the organic chemist with a hardy challenge. Cations are usually discriminated on the basis of charge and size. Anions of interest, as, for example, oxoanions, are often multiatomic structures with a delocalisation of the negative charge over a rather complex molecular geometry. This complexity and varied physical properties—anions are larger than cations being spherical, linear planar, tetrahedral or octahedral—have to be taken into account for the design of molecular systems to selectively recognise an anion via the introduction on anionic receptors of specific binding sites.[1] Synthetic anion receptors based on calixarenes have been divided into inorganic and organic classes.[1] Among them charged systems have been reported in which a combination of electrostatic forces and secondary binding elements are responsible for anion binding. Oxoanions have been extracted from water into chloroform by calixarenes substituted with alkylammonium units.[2–4] Selective extraction of chromate and dichromate was observed but the nature of extracted species was not determined.[2,3] Selective extraction of selenite and selenate has been used to selectively preconcentrate trace amounts of selenate with no characterisation of the extracted species.[4]

In the present note, we report the synthesis of 1,3-dibutyltriphenylphosphonium *p-tert*-butyl calix[4]arene derivative **2**.

The synthesis of **2** was carried out by two different ways given in Scheme 1.[5] In a preliminary step (pathway A) *p-tert*-butyl calix[4]arene was reacted with a large excess of 1,4-dibromobutane in the presence of 1 equiv of K_2CO_3 in refluxing acetone for 16 h. 1,3-Subsequently dibutylbromo *p-tert*-butyl calix[4]arene **1** was reacted with 3 equiv of triphenyl phosphine in refluxing chloroform for 1 week. 1,3-Dibutyltriphenylphosphonium *p-tert*-butyl calix[4]arene **2** precipitated during evaporation of the solvents. Similar reactions with shorter 1,3-diethylbromo- and 1,3-dipropylbromo *p-tert*-butyl calix[4]-arenes failed probably due to steric hindrance. In different pathway B, **2** was directly prepared by reaction of *p-tert*-butyl calix[4]arene with 2 equiv of commercial 4-bromobutyltriphenylphosphonium bromide in the presence of 1 equiv of K_2CO_3 in refluxing acetonitrile for 9 h. Compound **2** was obtained pure after precipitation during cooling and evaporation of the solvents. All the analytical data were in agreement with the proposed structures **1** and **2**. The 1,3-dialkylated structure and the cone conformation of **1** and **2** were deduced from their ^{1}H NMR spectrum. Two sets of two singlets were observed for the Ar*H* and for the C(C*H*$_3$)$_3$ groups. The

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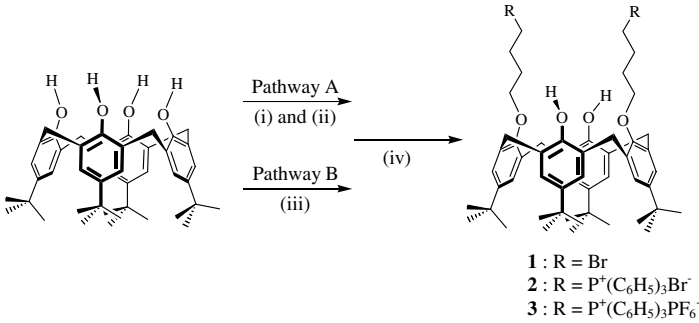

Scheme 1. Synthetic pathways A and B to **1**. Reagents and conditions: (i) $BrCH_2CH_2CH_2CH_2Br$, K_2CO_3, acetone, reflux, 16 h; (ii) $P(C_6H_5)_3$, chloroform, reflux, 7 days; (iii) $BrCH_2CH_2CH_2CH_2P^+(C_6H_5)_3Br^-$, K_2CO_3, acetonitrile, reflux, 9 h; (iv) $NaPF_6$ in $CHCl_3$.

ArCH_2Ar displayed characteristic AB systems at 3.82 and 4.24 ppm with $J = 12.8$ Hz for **1** and at 3.19 and 3.90 ppm with $J = 12.8$ Hz for **2**. The high symmetry of ligand **2** was also deduced from its $^{31}P\{^1H\}$ NMR spectra showing a lone singlet at 24.93 ppm ($CDCl_3$) and 25.05 ppm (CD_3OD) for $P^+(C_6H_5)_3$ falling in the expected range of values for triphenylphosphonium compounds ($^{31}P\{^1H\}$ NMR δ at 25.79 ppm for the $P^+(C_6H_5)_3$ of 4-bromobutyltriphenylphosphonium). The molecular formula was found to be $C_{88}H_{100}O_4P_2Br_2$ (MW = 1443.52) in which $2Br^-$ are already complexed. The FAB(+)MS spectrum of **2** indicated the loss of $1Br^-$ ($m/z = 1363.7$) and $2Br^-$ ($m/z = 1281.8$) and $m/z = 641.4$ because of the **2** positive charges. For the efficient anion complexation, **2** was treated with $NaPF_6$ in chloroform. The precipitate was filtered off and the solvent was removed and dried in vacuum to give **3**.

The binding properties of **2** and **3** towards anions were investigated by both ^1H and $^{31}P\{^1H\}$ NMR techniques into two different ways: (a) complexation of anions in methanol and (b) complexation of the same anions in chloroform. For way (a), CH_3OH solutions (10^{-2} M) of **2** were stirred with 10 equiv of anions salts: TBA(tetrabutylammonium)Cl, TBABr, $TBAHSO_4$, $TBACH_3CO_2$, $TBAH_2PO_4$, KSCN, $KClO_4$ and $K_2Cr_2O_7$ for 72 h at room temperature. After filtration (suspension was observed in the case of $KClO_4$ and $K_2Cr_2O_7$), the solvents were evaporated to dryness under vacuum. The resulting solids were dissolved in CD_3OD and ^1H and $^{31}P\{^1H\}$ NMR spectra were taken. Changes were only observed in the aromatic region of the ^1H NMR spectra. Figure 1 shows the chemical shifts in the aromatic region in the case of free ligand **2** and in the presence of KSCN. One can see that the aromatic protons $P^+(C_6H_5)_3$ are changed to give a more well-resolved spectrum in the presence of KSCN. This may be due to a better binding of SCN^- (which is the best bounded anion in the series) compared to Br^- and indicated the existence of phosphonium-anion electrostatic and/or π-anion forces.

At the same time the $^{31}P\{^1H\}$ NMR signal of $P^+(C_6H_5)_3$ lightly shifted from 25.05 to 24.89 ppm (KSCN), 25.03 ppm ($KClO_4$) and 24.95 ppm ($KReO_4$). Figure 2 shows the signal of $P^+(C_6H_5)_3$ of **2** before and after complexation of KSCN.

In the case of KSCN we have been able to show evidence of complexation of SCN^- by the FAB-mass spectrometry. A peak at $m/z = 1340.6$ was detected corresponding to the molecular weight of **2**$-Br^-+SCN^-$. Macrocyclic effect was demonstrated by reacting the 1,3-O-dialkylated calixarene derivative **4**, related to **2**, bearing one *n*-butyltriphenylphosphonium and one *n*-butyl arms with which no extraction in $CDCl_3$ was detected. For way (b), $CDCl_3$ solutions (10^{-3} M) of **3** were treated at room temperature with an excess of the same anions salts. Changes in the ^1H and $^{31}P\{^1H\}$ NMR spectra were observed for all anions tested. Both ^1H and $^{31}P\{^1H\}$ NMR spectra were in agreement to conclude

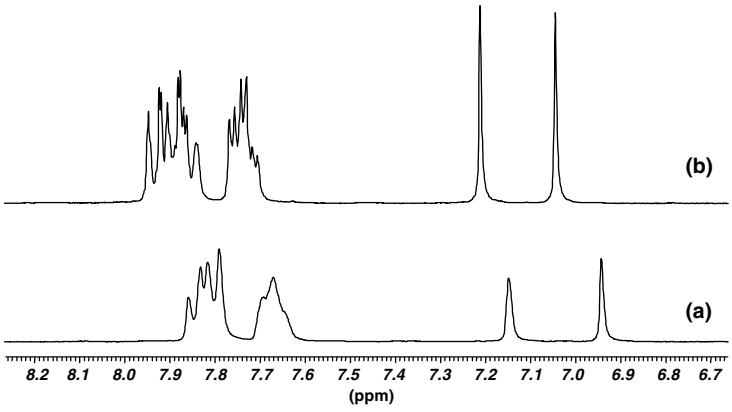

Figure 1. ^1H NMR spectrum in CD_3OD of the aromatic region of (a) **2** and (b) in the presence of an excess of KSCN.

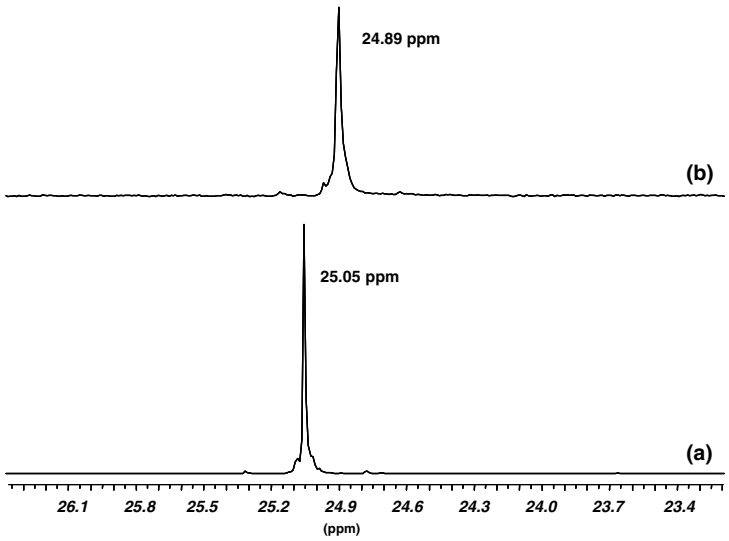

Figure 2. $^{31}P\{^{1}H\}$ NMR spectrum in CD_3OD of (a) **2** and (b) in the presence of an excess of KSCN.

that the anion is located close to the positively charged $P^{+}(C_6H_5)_3$. In particular, the broad peak at 3.26 ppm corresponding to the methylenic protons $CH_2P^{+}(C_6H_5)_3$ in the ^{1}H NMR spectra of **3** shifted to 4.05 (TBACl), 3.89 (TBABr), 3.67 ($TBAHSO_4$), 3.88 ppm ($TBACH_3CO_2$), 4.03 ppm ($TBAH_2PO_4$), 3.65 ppm (KSCN) and 3.38 ppm ($KClO_4$). Figure 3 shows the changes of the ^{1}H NMR chemical shifts in the methylene region of **3** in $CDCl_3$ in the presence of an excess of KSCN.

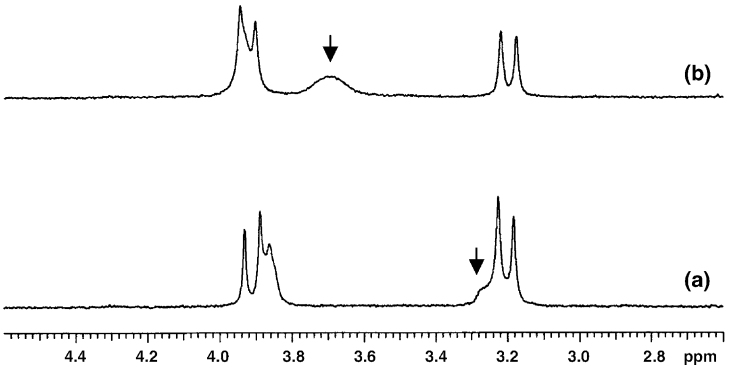

Figure 3. ^{1}H NMR spectrum in $CDCl_3$ of the methylenic region (the arrows denotes the methylene $CH_2P^{+}(C_6H_5)_3$) of (a) **3** and (b) in the presence of an excess of KSCN.

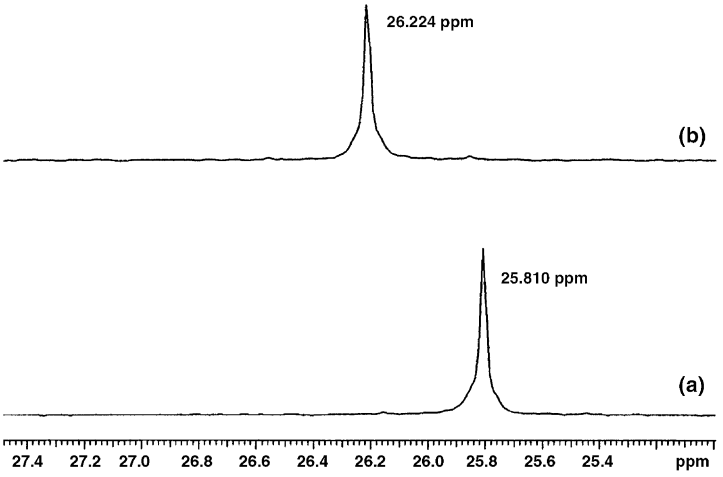

Figure 4. $^{31}P\{^{1}H\}$ NMR spectrum in $CDCl_3$ of (a) **3** and (b) in the presence of an excess of $TBAHSO_4$.

Table 1. Compound **3**: anion stability constant data from titration in $CDCl_3$

Anion	K_a	Error (%)
ClO_4^-	194	15
CH_3COO^-	215	4
Br^-	226	7
Cl^-	251	15
HSO_4^-	602	12
$H_2PO_4^-$	750	16

Similarly, changes were observed in the $^{31}P\{^1H\}$ NMR in this solvent indicating the complexation effectively occurred at the phosphonium centres. The signal of $P^+(C_6H_5)_3$ in the $^{31}P\{^1H\}$ NMR spectra shifted from 25.81 to 26.22 ppm ($TBAHSO_4$), and 25.90 ppm ($KClO_4$), respectively. Figure 4 shows the shift of the signal of $P^+(C_6H_5)_3$ of **3** in the absence and presence of $TBAHSO_4$.

The observed shifts were larger in $CDCl_3$ than in CD_3OD probably because methanol is more solvating than chloroform and electrostatic interactions between the phosphonium centres and the anions are weaker.

We therefore determined the stability constants of ligand **3** with anions in $CDCl_3$. The addition of TBA anion salts provoked $\Delta\delta$ of $CH_2P^+(C_6H_5)_3$ protons resulting in titration curves suggesting **3** forms 1:1 stoichiometric solution complexes with various anions. The nonlinear curves fitting program EQ-NMR[6] gave the different anion stability constants presented in Table 1.

The order of magnitude of the K_a values seems to indicate the preference of **3** for tetrahedral anions with OH functions leading to possible involvement of hydrogen bonding. Hydrogen bonding may occur with another anion and/or could be due to the formation of dimeric structures.

Further work is directed towards: (a) the synthesis of [2 + 2′] mixed functionalised calix[4]arenes consisting of positively charged groups of different nature (phosphonium–ammonium), (b) the complexation of organic anions and (c) the use of these new receptors in supramolecular technologies.

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5. *General*. Melting points (mps), Büchi 500. ^1H NMR, Bruker SY 200 (δ in ppm, J in Hz). ^{31}P NMR, 300 MHz (δ in ppm). FAB(+)MS spectra were obtained on a VG-Analytical ZAB HF. Elemental analyses were performed at the Service de Microanalyse of the Institut de Chimie de Strasbourg. All the reactions were run under nitrogen atmosphere. All reagents were commercial and used without further purification.
   Pathway A. (i) *1,3-Butyldibromo p-tert-butyl calix[4]arene* **1**. *p-tert*-Butyl calix[4]arene (4.943 g; 7.62 mmol), K_2CO_3 (1.051 g; 7.62 mmol), 1,4-dibromobutane (5.015 g; 22.80 mmol), acetone (200 mL) were refluxed under nitrogen for 16 h. After evaporation of the solvents, the residue was precipitated with methanol. Compound **1** (4.568 g) was obtained pure as a white solid. Mp > 280 °C (decomposition). ^1H NMR ($CDCl_3$): δ 7.40 (s, 2H, O*H*), 7.06 (s, 4H, Ar*H*), 6.80 (s, 4H, Ar*H*), 4.24 (d, $J = 12.8$ Hz, 4H, ArCH_2Ar), 4.01 (t, $J = 6.0$ Hz, CH_2Br), 3.64 (t, $J = 6.4$ Hz, 4H, CH_2OAr), 3.32 (d, $J = 12.8$ Hz, ArCH_2Ar), 2.35 (quint., $J = 6.7$ Hz, 4H, CH_2CH$_2$Br), 2.20 (quint., $J = 6.7$ Hz, 4H, CH_2CH$_2$OAr), 1.30 (s, 18H, C(CH_3)$_3$), 0.96 (s, 18H, C(CH_3)$_3$). Yield 80%. (ii) *1,3-Butylditriphenylphosphonium p-tert-butyl calix[4]arene* **2**. 1,3-Dibromo calix[4]arene **1** (1.055 g; 1.15 mmol), triphenyl phosphine (0.905 g; 3.45 mmol), chloroform (8 mL) were refluxed for 1 week under nitrogen. Compound **2** (1.505 g) was obtained pure as a white solid by precipitation with acetone. Mp > 280 °C (decomposition). ^1H NMR ($CDCl_3$): δ 7.89–7.58 (m, 30H, P$^+$(C$_6$H$_5$)$_3$), 7.48 (s, 2H, O*H*), 6.99 (s, 4H, Ar*H*), 6.79 (s, 4H, Ar*H*), 3.98 (br t, $J = 10.9$ Hz, CH_2P$^+$(C$_6$H$_5$)$_3$), 3.92 (t, $J = 6.8$ Hz, 4H, CH_2OAr), 3.90 (d, $J = 12.8$ Hz, ArCH_2Ar), 3.19 (d, $J = 12.8$ Hz, 4H, ArCH_2Ar), 2.21–2.16 (m, 8H, ArOCH$_2$CH_2CH_2CH$_2$ P$^+$(C$_6$H$_5$)$_3$), 1.28 (s, 18H, C(CH_3)$_3$), 1.00 (s, 18H, C(CH_3)$_3$). ^{31}P NMR ($CDCl_3$): δ 25.93. ^1H NMR (CD_3OD): δ 7.85–7.67 (m, 30H, P$^+$(C$_6$H$_5$)$_3$), 7.14 (s, 4H, Ar*H*), 6.94 (s, 4H, Ar*H*), 4.04 (d, $J = 13.3$ Hz, ArCH_2Ar), 4.01 (large s, $J = 10.9$ Hz, CH_2P$^+$(C$_6$H$_5$)$_3$), 3.59 (br t, $J = 12.9$ Hz, 4H, CH_2OAr), 3.54 (d, $J = 13.3$ Hz, 4H, ArCH_2Ar), 2.15–2.08 (m, 8H, ArOCH$_2$CH_2CH_2CH$_2$ P$^+$(C$_6$H$_5$)$_3$), 1.30 (s, 18H, C(CH_3)$_3$), 1.01 (s, 18H, C(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 25.05. FAB(+)MS calcd for $C_{88}H_{100}O_4P_2Br_2$: 1443.52, $m/z = 1363.7$ (M$^+$−Br$^-$), 1281.8 (M$^+$−2Br$^-$), 641.4 (M$^+$−2Br$^-$/2). Yield 90%.
   Pathway B. (iii) *1,3-Butylditriphenylphosphonium p-tert-butyl calix[4]arene* **2**. *p-tert*-Butyl calix[4]arene (0.203 g; 0.48 mmol), K_2CO_3 (0.068 g; 0.492 mmol), 4-bromobutyltriphenylphosphonium bromide (0.472 g; 0.98 mmol), acetonitrile (30 mL) were refluxed under nitrogen for 20 h. Compound **2** precipitated directly in the reacting medium. Quantitative yield.
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