Supporting Information

for

Angew. Chem. Int. Ed. Z50941

© Wiley-VCH 2003
69451 Weinheim, Germany
Calix\([n]\)bipyroles: Synthesis, Characterization, and Anion Binding Studies

Jonathan L. Sessler*, Deqiang An, Won-Seob Cho, and Vincent Lynch

Department of Chemistry and Biochemistry, Institute for Cellular and Molecular Biology

1 University Station - A5300, The University of Texas at Austin,

Austin, TX 78712-0165 (USA)

Experimental

\(^1\)H NMR titration studies

ITC titration studies

**Experimental**

**Calix[3]bipyrrrole 10 and calix[4]bipyrrrole 11.** 2,2’-Bipyrrole (0.2 g, 1.5 mmol) was dissolved in methanol (15 mL) and the mixture was degassed by bubbling with Ar for 10 minutes. Acetone (88 mg, 1.5 mmol) was added and the mixture was stirred for another 5 minutes at room temperature. Methanesulfonic acid (73 mg, 0.75 mmol) was added, with the resulting mixture stirred at room temperature for 2 hours. Saturated sodium bicarbonate (aq) (30 mL) was added to quench the reaction, followed by extraction with dichloromethane (90 mL). The organic phase was washed with water (30 mL), dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. The residue obtained was then purified by column chromatography over silica gel (eluent: dichloromethane for \(10\), followed by dichloromethane-ethyl acetate 98:2 v/v for \(11\)) to afford \(10\) and \(11\):
For 10: pale green solid (63 mg, 24%); m.p. > 200 °C (decomp.); $^1$H-NMR (400 MHz, CD$_3$CN, 25 °C) δ 1.61 (s, 18 H, meso-CH$_3$), 5.95 (t, 6H, β-pyrrole CH), 6.03 (t, 6H, β-pyrrole CH), 8.52 (s, 6H, pyrrole-NH); $^{13}$C-NMR (100MHz, CD$_3$CN, 25 °C) δ 29.5, 36.1, 104.0, 104.7, 125.4, 138.9; HR-MS (Cl$^+$) m/z (M + H$^+$) calcd. for C$_{33}$H$_{37}$N$_6$: 517.3079, found: 517.3069.

For 11: pale green solid (75 mg, 29%); m.p. > 200 °C (decomp.); $^1$H-NMR (400 MHz, CD$_3$CN, 25 °C) δ 1.56 (s, 24 H, meso-CH$_3$), 5.91 (t, 8H, β-pyrrole CH), 5.99 (t, 8H, β-pyrrole CH), 8.42 (s, 8H, pyrrole-NH); $^{13}$C-NMR (100MHz, CD$_3$CN, 25 °C) δ 29.1, 35.7, 102.5, 104.8, 125.6, 138.4; HR-MS (Cl$^+$) m/z (M$^+$) calcd for C$_{44}$H$_{48}$N$_8$: 688.4001, found: 688.3998.
\textbf{\textsuperscript{1}H NMR Titration Studies}

Proton NMR-based titration studies were carried out using a Varian Unity Plus 400 MHz NMR spectrometer. The receptors, as $2.0 \times 10^{-3}$ M solutions, were titrated by adding known quantities of concentrated solution of the anions in question (in the form of their tetrabutylammonium salts). All tetrabutylammonium anions were purchased from Fluka and used without further purification. The anion solutions used to effect the titration contained the receptors at a concentration of $2.0 \times 10^{-3}$ M to account for dilution effects during the titrations. The data were fit to a 1:1 binding profile according to the method of Wilcox (Wilcox, C. S. in \textit{Frontiers in Supramolecular Organic Chemistry and Photochemistry}; Schneider, H. J., Dürr, H., Eds.; VCH: Weinheim, 1991) using the changes in the pyrrolic NH resonances in the \textsuperscript{1}H NMR spectra. DMSO-$d_6$ and acetonitrile-$d_3$ were purchased from Cambridge Isotope Laboratories, Inc. and dried over molecular sieves (4Å) before use.
Fig. 1 $^1$H NMR titration curve for compound 10 and chloride ion in DMSO-$d_6$. $[10] = 2.0 \times 10^{-3}$ M. $[\text{TBACl}] = 0 - 6.5 \times 10^{-3}$ M. The curve shows the fit of the experiment data to a 1:1 binding profile.

Fig. 2 Job Plot for the binding of compound 10 and chloride ion in DMSO-$d_6$. 

Model: NMR_Wilcox_1 to1

\[ K = 14922.88509 \pm 1823.65138 \]
Fig. 3  $^1$H NMR titration curve for compound 10 and bromide ion in DMSO-$d_6$. $[10] = 2.0 \times 10^{-3}$ M. $[\text{TBABr}] = 0 - 3.2 \times 10^{-2}$ M. The curve shows the fit of the experiment data to a 1:1 binding profile.

Fig. 4  Job plot for the binding of compound 10 and bromide ion in DMSO-$d_6$. 

Model: NMR_Wilcox_1to1

$K = 455.88891 \pm 14.10695$
Fig. 5 $^1$H NMR titration curve for compound 10 and iodide ion in CD$_3$CN. [10] = 2.0 × 10$^{-3}$ M. [TBAI] = 0 – 3.2 × 10$^{-2}$ M. The curve shows the fit of the experiment data to a 1:1 binding profile.

Fig. 6 Job plot for the binding of compound 10 and iodide ion in CD$_3$CN.
Due to difficulties in determining the exact concentrations of the free host, the complex of the host with chloride ion, and the free chloride ion, no binding constants for the slow exchange inferred from these spectra were calculated.
1H NMR spectra observed when compound 10 at a concentration of 2 × 10⁻³ M was titrated with Bu₄NBr in CD₃CN

Due to difficulties in determining the exact concentrations of the free host, the complex of the host with chloride ion, and the free chloride ion, no binding constants for the slow exchange inferred from these spectra were calculated.
ITC Titration Studies

Microcalorimetric titration (experimental temperature: 30 °C) was performed using an Isothermal Titration Calorimeter (ITC) purchased from Microcal Inc., MA. The ORIGN software provided by Microcal Inc. was used to calculate the binding constant ($K_a$) and the enthalpy change ($\Delta H$). DMSO and CH$_3$CN were spectral grade (Aldrich) and not otherwise dried before use.

**Compound 10 titrated with Bu$_4$NCl in CH$_3$CN**
Compound 10 titrated with Bu₄NBr in CH₃CN
Compound 10 titrated with Bu₄NCl in DMSO
Compound 10 titrated with Bu₄NBr in DMSO