Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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Hidekazu Miyaji[a]; Deqiangan An[a]; Jonathan L. Sessler
[a] Department of Chemistry and Biochemistry and Institute for Cellular and Molecular Biology, University of Texas af Austin, Austin, TX, USA

To cite this Article Miyaji, Hidekazu , An, Deqiangan and Sessler, Jonathan L.(2001) 'Mono Halogen Substituted Calix[4]pyrroles: Fine-tuning the Anion Binding Properties of Calix[4]pyrrole', Supramolecular Chemistry, 13: 6, 661 — 669
To link to this Article: DOI: 10.1080/10610270108027495
URL: http://dx.doi.org/10.1080/10610270108027495

Supramolecular Chemistry, Vol. 13, pp. 661–669
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Mono Halogen Substituted Calix[4]pyrroles: Fine-tuning the Anion Binding Properties of Calix[4]pyrrole

HIDEKAZU MIYAJI, DEQIANG AN and JONATHAN L. SESSLER*

Department of Chemistry and Biochemistry and Institute for Cellular and Molecular Biology, University of Texas at Austin, Austin TX 78712-1167, USA

Single halogen atom (i.e. I, Br, Cl and F) substituted calix[4]pyrroles, compounds 2, 3, 4 and 5, were synthesized. Studies of these systems reveal that replacement of a single β-pyrrolic hydrogen atom can increase the anion binding ability of calix[4]pyrroles for a variety of anions (e.g. Cl^-, Br^-, $H_2PO_4^-$ and HSO_4^-) relative to normal non-halogen substituted calix[4]pyrrole 1. In the case of chloride anion, the expected relative affinity sequence of 5 > 4 > 3 > 2 was observed. This was not found to be true for Br^-, $H_2PO_4^-$, and HSO_4^-. Here, the chlorine substituted calix[4]pyrrole 4 was found to display a slightly higher affinity in the case of each anion than the fluorine-bearing derivative 5. This was rationalized in terms of intermolecular NH · · · F hydrogen bonding interactions being present in CD_2Cl_2 solutions of 5. Support for this latter conclusion came from concentration and temperature-dependent NMR spectroscopic studies.

A matched set of mono halogen substituted calix[4]pyrroles was used to study in detail, the extent to which halogen substituents may be used to fine-tune the anion binding properties of calix[4]-pyrroles.

Keywords: Calix[4]pyrrole; Halogenation; Anion receptor; Macrocycle

INTRODUCTION

Anion recognition, an area with important potential applications, has emerged as a fast-evolving sub-field in supramolecular chemistry [1,2]. In 1996, our group reported that calix[4]-pyrrole [3] **1** is an effective neutral anion binding agent [4]. Since that time, a number of strategies for generating functionalized calix[4]pyrroles have been reported by our group [5–8] and that of Gale [9]. One of the more useful functionalization strategies involves replacement-type substitutions at one or more of β-pyrrolic positions (*C*-rim modification) [10]. This generalized approach is advantageous because calix[4]pyrrole **1** (available in one step from pyrrole and acetone) can be used as the starting material thus producing easily useful synthetic intermediates. For instance, we recently reported the synthesis of a mono-iodocalix[4]pyrrole **2** and its further elaboration to range of functionalized products

*Corresponding author. E-mail: suprachem@mail.cm.utexas.edu

using easy-to-effect Pd-catalyzed C–C bond forming procedures [11–13]. The replacement of a β-pyrrolic proton by a halogen atom is also potentially beneficial because it might allow the effect of substituents on the anion binding properties of calix[4]pyrroles to be studied in greater detail. Although the effect of eight β-pyrrolic bromo and fluoro substituents has been noted previously [10,14], we considered that further detailed insights could be obtained by studying systems bearing only a single substituent having different electronegativities (i.e. I, Br, Cl and F). In this paper, we report the synthesis of a matched set of mono halogen substituted calix[4]pyrroles, **2**–**5**, as well as their anion binding properties.

RESULTS AND DISCUSSION

Synthesis

The synthesis of the mono-iodocalix[4]pyrrole **2** has previously been reported [11,15]. This species was obtained by treating *meso*-octamethylcalix[4]pyrrole **1** with I_2 and $(CF_3CO_2)_2PhI$ in CH_2Cl_2 at R.T. (20%) or with *n*-butyllithium and ICI in THF at −78°C (7%). Its mono-bromo analogue **3** was synthesized by treating calix[4]pyrrole **1** with 1.2 equiv. of *N*-bromosuccinimide (NBS) in THF at 60°C (21%). The monochlorocalix[4]pyrrole **4** was synthesized in an analogous manner using 1.5 equiv. of *N*-chlorosuccinimide (NCS) in THF at 60°C (33%). The corresponding mono-fluoro derivative **5** was synthesized by treating calix[4]pyrrole **1** with 1.2 equiv. of *N*-fluoropyridinium triflate [16] in THF at 60°C (15%) (Scheme 1). All compounds were isolated by column chromatography and identified by mass spectrometry, NMR-spectroscopy and elemental analysis. With the exception of the mono-fluoro derivative **5** that showed evidence for intermolecular aggregation under certain conditions (see below), all compounds gave data that were in accord with their proposed structures. Further, in the case of **5**, weak $^{19}F-^{1}H$ splittings ($J = 3.3$ Hz) were also observed for the CH_{py} signals. Such splittings were not seen in the case of **2**, **3**, or **4**.

Small amounts of bis-halogen substituted calix[4]pyrrole products were also isolated in the course of the chromatographic separations. However, no attempt was made to purify these products, obtained as a mixture of isomers, to the point of homogeneity.

Anion Binding Properties

The solution phase anion binding properties of calix[4]pyrroles **2**–**5** were evaluated using ^{1}H NMR spectroscopic methods. Specifically, various anionic guests (tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$ or HSO_4^-) were added in a titration like fashion to solutions of **2**, **3**, **4** or **5** (5.0 mM) in CD_2Cl_2 with the shift in the calix[4]pyrrole NH (and/or β-pyrrolic CH) proton peaks being noted after each addition. Without exception, the addition of anions caused the pyrrole NH resonances to move to lower field. The actual extent of this downfield shift, however,

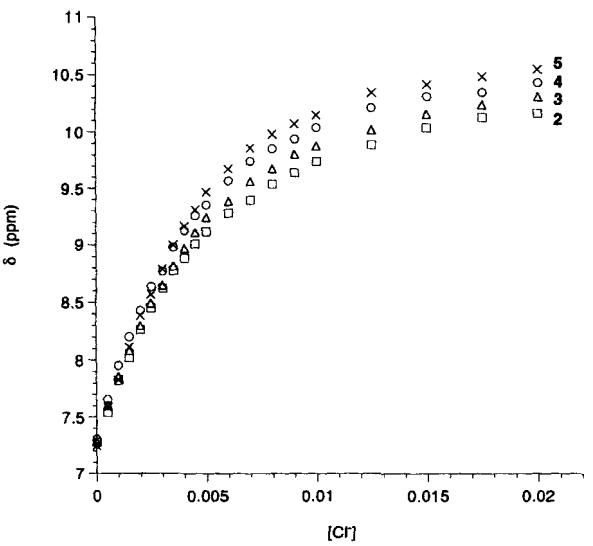
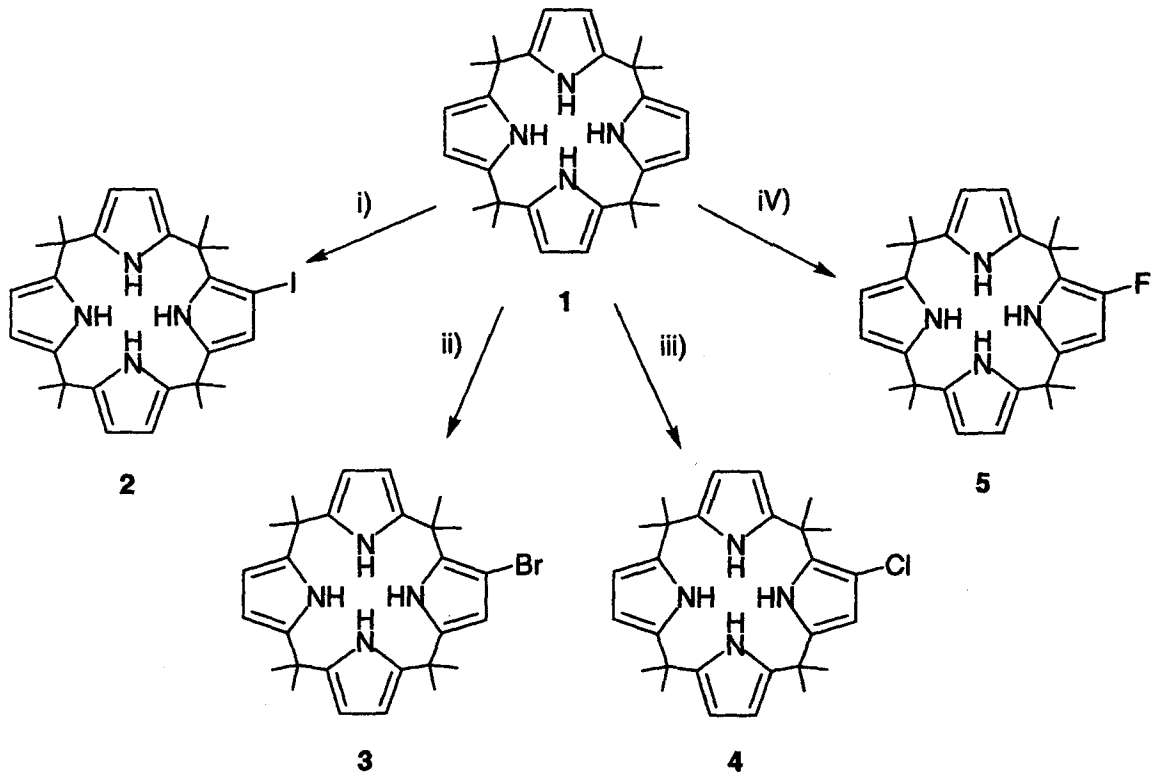


FIGURE 1 ^{1}H NMR spectroscopic titration curves of the halogen substituted calix[4]pyrrole **2**–**5** with Bu_4NCl in CD_2Cl_2 [Host]: 5.0 mM).



SCHEME 1

was found to be a function of anion concentration, receptor, and choice of anion. This point is illustrated in Fig. 1, which shows the chemical shifts of the pyrrole NH protons of compounds **2**–**5** observed upon the addition of up to 4 equiv. of tetrabutylammonium chloride. As can be seen by inspection of this figure, fewer chloride anion equivalents were required to saturate the binding profile in the case of the fluoro-(**5**), chloro-(**4**), bromo-(**3**), and iodo-(**2**) substituted calix[4]pyrroles, respectively. This is consistent with the fluorine functionalized calix[4]pyrrole showing the highest affinity for this particular anion. This is reflected in the association constants (K_a) as determined by standard non-linear curve fitting procedures [17,18] (*c.f.* Table I).

TABLE I Association constants (K_a) for compounds **1–5** * with anionic substrates† in CD_2Cl_2 at 298 K

Anion	K_a (M^{-1})				
	1	**2**	**3**	**4**	**5**
F^-	>10000‡	>10000	>10000	>10000	>10000
Cl^-	350‡	610	650	780	870
Br^-	10‡	49	53	80	62
I^-	<10‡	<5	<5	<5	<5
$H_2PO_4^-$	97‡	100	180	230	130
HSO_4^-	<10‡	<5	6	13	<5

*Estimated errors were <10%.
†Anions were added as their tetrabuthylammonium salts.
‡Data from Ref.[4].

The K_a values tabulated in Table I confirm what would be expected, namely that, as a general rule, the halogen substituted calix[4]pyrroles **2–5** bind anions more strongly than the all-hydrogen parent **1**. These same data also reveal that, while the fluoro derivative, as anticipated, displays the highest affinity for chloride anion (*vide supra*), it is actually the mono-chlorocalix[4]pyrrole **4** that binds bromide, dihydrogen phosphate and hydrogen sulfate anions most strongly. These findings, which are outside the limits of error, lead to the consideration that factors other than strict substituent electronegativity are controlling the anion affinities of, at least, receptor **5**. Based on the intermolecular NH· · ·F interactions observed in the solid state by X-ray diffraction analysis in the case of octafluorocalix[4]pyrole [14], the lower-than-expected anion affinities seen in the case of **5** are thought to reflect a competition between "narcissistic" intermolecular NH· · ·F hydrogen bonding interactions and NH· · ·A^- anion binding events (A^-=F^-,Cl^-, etc.).

Concentration and Temperature-dependent NMR Spectroscopic Studies of 5

In order to confirm the presence of the proposed intermolecular NH· · ·F hydrogen bonding interactions in the case of **5**, concentration dependent ^{1}H NMR spectroscopic studies were carried out in CD_2Cl_2 solution. One prototypical set of studies is reproduced in Fig. 2; it shows the concentration dependent ^{1}H NMR spectral changes observed for the four NH protons of **5** as the concentration of this mono-fluorocalix[4]-pyrrole is varied between 2.5 and 50 mM. At high calix[4]pyrrole concentrations, the NH peaks are shifted to slightly lower field. For example, the peaks appearing at 7.224, 7.138, 6.962, and 6.378 ppm at [**5**]=2.5 mM were found to resonate

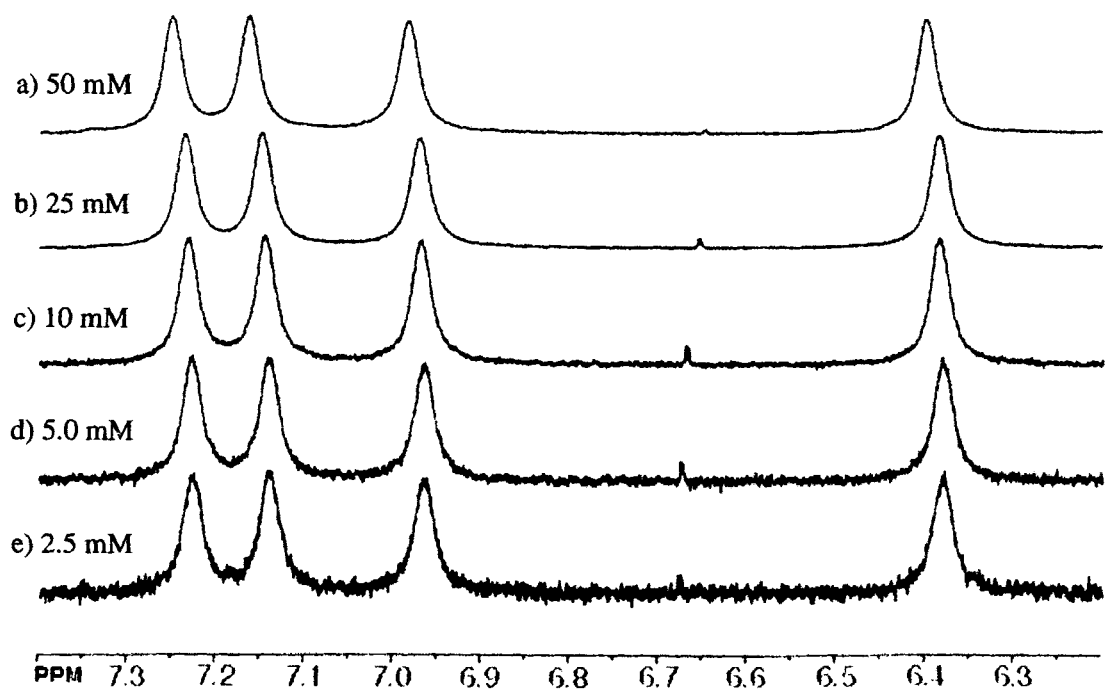


FIGURE 2 Concentration dependent ^{1}H NMR spectra showing the concentration dependent shifts observed for the four NH proton signals of mono-fluorocalix[4]pyrrole **5** (CD_2Cl_2, 298 K).

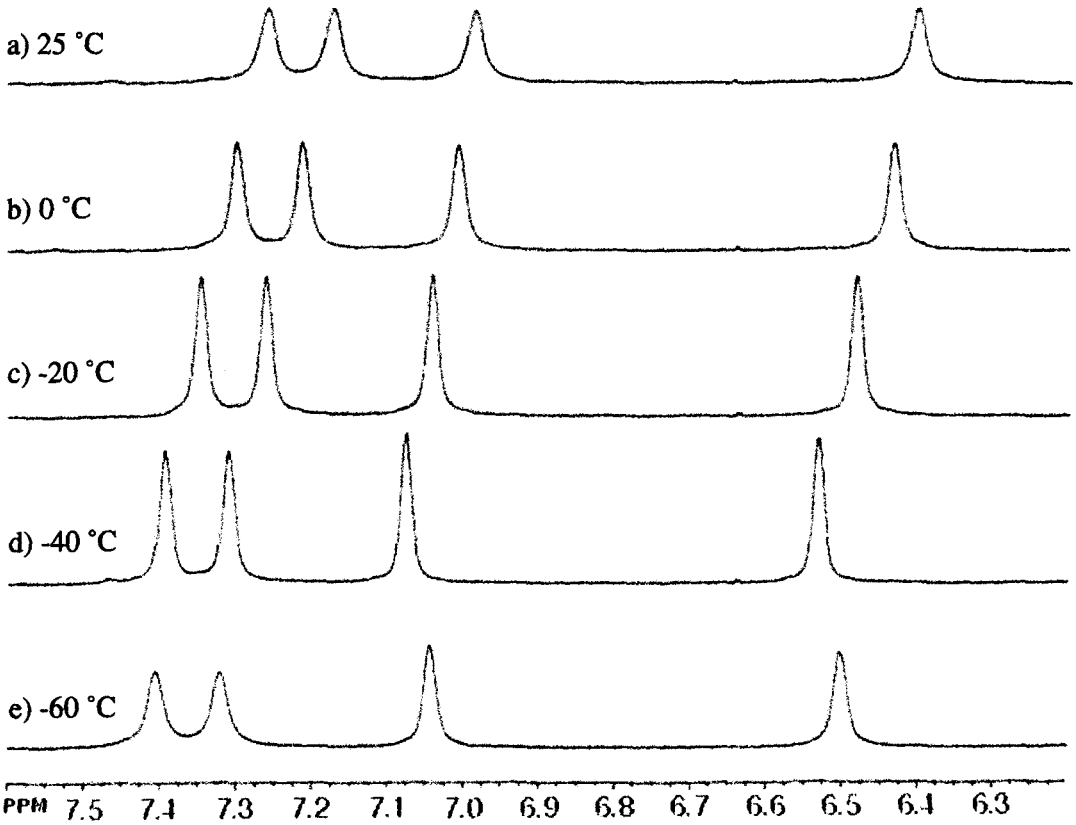


FIGURE 3 Temperature dependent ^{1}H NMR spectra showing the changes observed for the four NH proton signals of monofluorocalix[4]pyrrole **5** (CD_2Cl_2, 50 mM).

at 7.248, 7.161, 6.982, and 6.399 ppm when [5]=50 mM. While not a proof, these observations are consistent with the formation of NH· · ·F mediated dimers, or possibly aggregates, at higher concentrations.

Further insights into the solution phase behavior of **5** were obtained by carrying out temperature dependent ^{1}H NMR and ^{19}F NMR spectroscopic studies. As reproduced in Fig. 3, ^{1}H NMR spectral analysis of **5** reveals that the four NH peaks observed for 50 mM solutions of **5** in CD_2 Cl_2, appearing at 7.248, 7.161, 6.982, and 6.399 ppm at 25°C, are shifted to 7.392, 7.309, 7.075, and 6.531 ppm, respectively, at −40°C. Further cooling to −60°C, caused the two peaks resonating at 7.392, and 7.309 ppm at −40°C to shift even further downfield to 7.405 and 7.320 ppm, respectively. On the other hand, the two peaks appearing at 7.075 and 6.531 ppm at −40°C were found to be shifted "back" upfield to 7.043 and 6.503 ppm. ^{19}F NMR spectral analysis of **5** reveals that the ^{19}F peak observed for 50 mM solution of **5** in CD_2Cl_2, appearing at −165, 18 ppm at 0°C, is shifted to −165.12, −165.04, −164.95, and −164.83 ppm, at −20, −40, −60 and −80°C, respectively.

The downfield shifts of the NH and ^{19}F NMR peaks of **5** observed at high concentration and low temperature are consistent with the proposed NH· · ·F hydrogen bonding. Such interactions are expected to remove electronic density from the β-pyrrolic positions and lead to increasing downfield shifts as the degree of interaction becomes stronger. Lowering the temperature is expected to enhance the NH· · ·F interaction, and thereby increase the

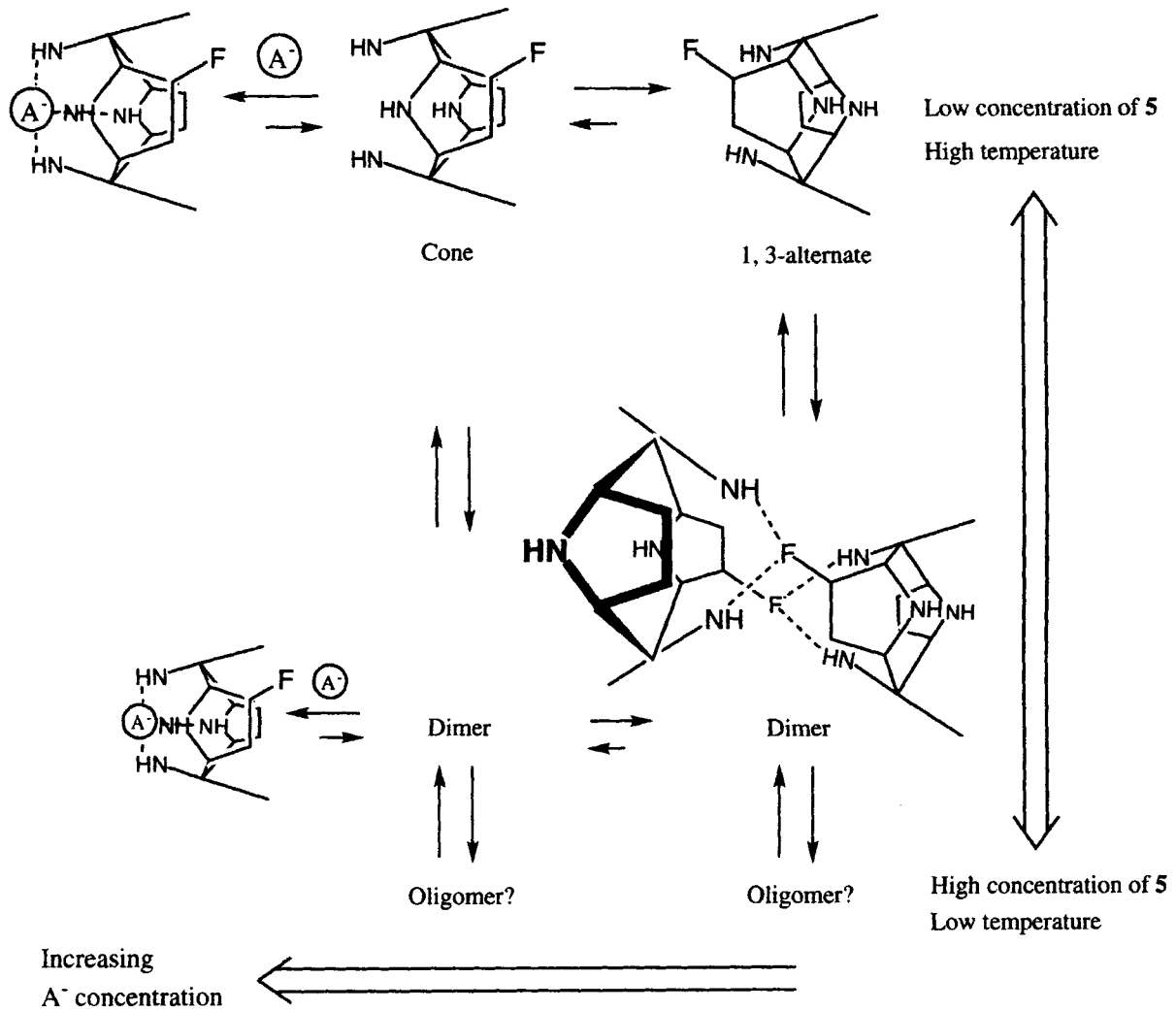


FIGURE 4 Schematic showing the proposed intermolecular NH· · ·F hydrogen bonding- mediated self-organization and anion recognition characteristics of mono-fluorocalix[4]pyrrole 5.

extent of the downfield shift. This is what is seen by experiment for the ^{19}F signal and for all of the NH signals down to at least −40°C. However, as the temperature is lowered further, two of the NH proton resonances shift upfield, as noted above. This might be ascribed to a freezing out of the more stable 1,3-alternate conformation from among the mixture of rapidly inter-converting cone, partial cone, 1,2-alternate and 1,3-alternate conformers that exist in the absence of anions or other conformation "locking" stimuli. These two equilibria, intermolecular hydrogen bonding and conformational locking, are illustrated schematically (as is anion binding) in Fig. 4. This figure helps explain how as the result of NH· · ·F induced electron withdrawing and adjacent pyrrole-derived ring current effects, two of the four NH signals shift first to lower field and then "back" up to somewhat higher field as the temperature is lowered from room temperature down to −60°C. Here the key point is that, at a low temperature, the 1,3-alternate dimeric form of **5** is expected to dominate. In this proposed dimer, the most stable of the many species in

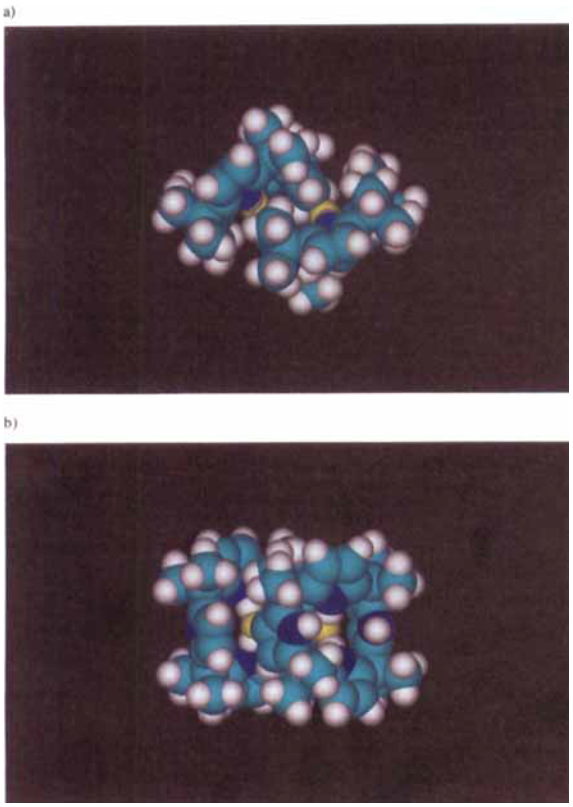


FIGURE 5 Schematic representation of the 1,3-alternate dimer of **5** showing (a) top view and (b) side views. This model was generated using a commerically available software package [19].

rapid equilibrium at higher temperature, two of the four NH protons on each monomeric subunit are expected to interact with fluorine atoms and undergo shifts to lower field. On the other hand, the other two pyrrole NH protons are expected to experience ring current effects as the result of adjacent pyrroles. This point is illustrated in Fig. 5, which shows an idealized representation of the proposed 1,3-alternate dimeric form of **5**[19].

CONCLUSIONS

In conclusion, a series of halogen atom substituted calixpyrroles **2**–**5** were synthesized and their anion binding characteristics evaluated. In the case of chloride anion as a substrate, the mono-fluorocalix[4]pyrrole **5** displayed the highest affinity. On the other hand, bromide, dihydrogen phosphate and hydrogen sulfate anions were bound more strongly by the monochloro derivative **4**. These disparate results are rationalized in terms of intermolecular NH· · ·F hydrogen bonding interactions in the case of **5**. Specifically, in dichloromethane solution, the presence of these interactions is expected to interfere with anion binding. In the case of strongly bound anions, such as F^- and Cl^-, the resulting reduction in affinity is not sufficient to overcome the extra "boost" the presence of a fluorine substituent provides. However, this is apparently not the case for more weakly bound substrates such as Br^-, I^-, $H_2PO_4^-$ and HSO_4^-. Here, the interference due to intermolecular NH· · ·F interactions serves to reverse the inherent affinities and make **5** a weaker receptor than **4**. Independent of such rationales, the present results serve to underscore how halogenation of the β-pyrrolic positions may be used to fine-tune the anion binding abilities of calix[4]pyrroles.

EXPERIMENTAL

Materials and Instruments

All solvents were purchased from EM Science. Dichloromethane and THF were dried and distilled before use. All reagents were purchased from Aldrich Chemical Co. and used without further purification. *Meso*-octamethylcalix[4]pyrrole **1** was prepared using standard procedure [3] and purified by column chromatography over silica gel (eluent: dichloromethane/hexane; 1:1). TLC analyses were carried out using Whatman K6F silica get 60 Å (Plate thickness 0.25 mm). Column chromatography was performed on Whatman silica gel 60 Å (230–400 mesh). Proton and ^{13}C NMR spectra were recorded on a Varian 500 MHz spectrometer. Chemical shifts are

reported on the δ scale and referenced to solvent peaks. Coupling constants (J) are reported in hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Bell and Howell 21-110B instrument. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA.

Iodocalix[4]pyrrole (2)

Meso-octamethylcalix[4]pyrrole **1** (100 mg, 0.23 mmol) was dissolved in dry dichloromethane (10 ml). Bis-(trifluoroacetoxy) iodobenzene (83 mg, 0.19 mmol) and iodine (40 mg, 0.16 mmol) were then added to the solution. The reaction mixture was stirred for 10 min at room temperature under Ar. After passing through a small amount of silica gel (eluent: CH_2Cl_2), the solvent was evaporated off using a rotary evaporator. The residue was purified by column chromatography over silica gel (eluent: dichloromethane/hexane; 1:1). The fraction displaying an $R_f = 0.55$ on TLC (eluent: dichloromethane/hexane; 1:1) was isolated. (The starting material **1** has an $R_f = 0.5$) Yield: 26 mg (20%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.28 (s, 2H, NH), 6.93 (s, 2H, NH), 6.06 (d, 1H, $J = 3.0$ Hz, CH_{py}), 5.97–5.82 (m, 6H, CH_{py}), 1.67 (s, 6H, CH_3), 1.52 (12H, CH_3), 1.45 (s, 6H, CH_3), ^{13}C NMR(125 MHz, CD_2Cl_2) δ: 139.46, 139.33, 139.12, 138.84, 138.66, 137.94, 137.55, 136.14, 114.35, 104.48, 104.28, 104.01, 103.20, 103.14, 102.09, 54.87, 37.06, 35.55, 35.49, 35.38, 29.52, 28.76, 28.68, 28.47. HRMS (CI^+) calcd. for $C_{28}H_{35}IN_4$ 554.1906; found 554.1896. Anal. Calcd. for $C_{28}H_{35}IN_4$: C, 60.65; H, 6.36; N, 10.10. Found: C, 60.65; H, 6.35; N, 9.90.

Bromocalix[4]pyrrole (3)

Meso-octamethyl calix[4]pyrrole **1** (100 mg, 0.23 mmol) was dissolved in dry THF (10 ml). *N*-bromosuccinimide (NBS; 50 mg, 0.28 mmol) was then added to the solution. The reaction mixture was stirred for 5 h at 60°C under Ar. The solvent was evaporated off using a rotary evaporator. The residue was then purified by column chromatography over silica gel (eluent: dichloromethane/hexane; 1:1). The fraction displaying an $R_f = 0.54$ on TLC (eluent: dichloromethane/hexane; 1:1) was isolated. (The starting material **1** has an $R_f = 0.50$.) Yield: 25 mg (21%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.29(s, 2H, NH), 6.94 (s, 1H, NH), 6.83(s, 1H, NH), 5.96–5.82 (m, 7H, CH_{py}), 1.64 (s, 6H, CH_3), 1.51 (s, 12H, CH_3), 1.45 (s, 6H, CH_3). ^{13}C NMR (125 MHz, CD_2Cl_2) δ:139.43, 139.28, 138.65, 137.97, 137.48, 137.45, 137.42, 132.95, 108.75, 104.49, 104.22, 103.96, 103.15, 103.06, 102.07, 90.92, 36.88, 35.43, 35.33, 28.73, 28.64, 28.00. HRMS (CI^+) calcd. for $C_{28}H_{35}BrN_4$ 506.2045; found 506.2049. Anal. Calcd. for $C_{28}H_{35}BrN_4 \cdot 0.5H_2O$: C, 65.11;H, 7.03;N, 10.85. Found: C, 65.20; H, 6.90; N, 10.72.

Chlorocalix[4]pyrrole (4)

Meso-octamekthylcalix[4]pyrrole **1** (100 mg, 0.23 mmol) was dissolved in dry THF (10 ml). *N*-chlorosuccinimide (NCS; 45 mg, 0.34 mmol) was then added to the solution. The reaction mixture was stirred for 3 h at 60°C under Ar. The solvent was then evaporated off. The residue was purified by column chromatography over silica gel (eluent: dichloromethane/hexane; 1:1). The fraction displaying an $R_f = 0.53$ on TLC (eluent: dichloromethane/hexane; 1:1) was isolated. (The starting material **1** has an $R_f = 0.05$.) Yield: 35 mg (33%), ^{1}H NMR (500 MHz., CD_2Cl_2) δ: 7.30 (s, 1H, NH), 7.27 (s,1H,NH), 6.94(s, 1H, NH), 6.73(s, 1H, NH), 5.96–5.83(m, 7H, CH_{py}), 1.64(s, 6H, CH_3), 1.51(s, 12H, CH_3) 1.45(s, 6H, CH_3). ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 139.40, 139.24, 138.68, 138.07, 137.60, 137.42, 136.57, 131.30, 106.57, 106.03, 104.45, 104.14, 103.91, 103.16, 103.03, 102.14, 36.64, 35.62, 35.42, 35.33, 29.41, 28.75, 28.66, 27.87. HRMS (CI^+) calcd. for $C_{28}H_{35}ClN_4$ 463.2628; found 463.2619. Anal. Calcd. for $C_{28}H_{35}ClN_4 \cdot 0.5H_2O$: C, 71.24; H, 7.69; N, 11.87. Found: C, 71.46; H, 7.60; N, 11.81.

Fluorocalix[4]pyrrole (5)

Meso-octamethylcalix[4]pyrrole **1** (100 mg, 0.23 mmol) was dissolved in dry THF (20 ml). *N*-fluoropyridinum triflate (70 mg, 0.28 mmol) was then added to the solution. The reaction mixture was stirred for 0.5 h at 60°C under Ar. The solvent was then evaporated off. The residue was purified by column chromatography over silica gel (eluent: dichloromethane/hexane; 1:1). The fraction displaying an $R_f = 0.53$ on TLC (eluent: dichloromethane/hexane; 1:1) was isolated. (The starting material **1** has an $R_f = 0.50$.) Yield: 15 mg (15%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.25 (s, 1H, NH), 7.16 (s, 1H, NH), 6.99 (s, 1H, NH) 6.41(s, 1H, NH), 5.92–5.86 (m, 6H, CH_{py}), 5.71(d, 1H, $J = 3.3$ Hz, CH_{py}), 1.54 (s, 6H, CH_3), 1.51 (s, 12H, CH_3), 1.45 (s, 6H, CH_3). ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 147.99, 146.10, 139.15, 138.97, 138.95, 138.62, 138.15, 137.55, 134.19, 134.15, 118.47, 118.31, 104.16, 103.72, 103.50, 103.20, 102.96, 102.67, 93.56, 93.41, 35.61, 35.49, 35.46, 35.38, 30.05, 29.05, 28.83, 28.37, 28.35. HRMS (CI^+) calcd. for $C_{28}H_{35}FN_4$ 447.2924; found 447.2935. Anal. Calcd. for $C_{28}H_{35}FN_4$: C, 75.30; H, 7.90; N, 12.55. Found: C, 74.98; H, 7.97; N, 12.35.

Acknowledgements

This work was supported by the National Institutes of Health (Grant GM 58907) To J.L.S.

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