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Kai-Chi Chang

Tsuyoshi Minami

Petr Koutnik

Pavel Y. Savechenkov

Yuanli Liu

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Author(s)
Kai-Chi Chang, Tsuyoshi Minami, Petr Koutnik, Pavel Y. Savechenkov, Yuanli Liu, and Pavel Anzenbacher Jr.

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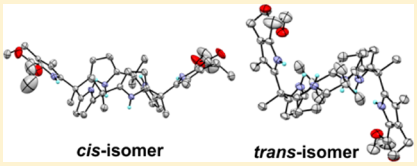
Anion Binding Modes in *meso*-Substituted Hexapyrrolic Calix[4]pyrrole Isomers

Kai-Chi Chang, Tsuyoshi Minami, Petr Koutnik, Pavel Y. Savechenkov, Yuanli Liu, and Pavel Anzenbacher, Jr.*

Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, United States

Supporting Information

ABSTRACT: We report on the synthesis of a new receptor for anions, *meso*-substituted hexapyrrolic calix[4]pyrrole **1**. The calix[4]pyrrole's core features two additional pyrrole side-arms suspended above or below the calix[4]pyrrole core. This hexapyrrolic calix[4]pyrrole **1** is formed as *cis*- and *trans*-configurational isomers, the structures of which have been determined by single crystal X-ray diffraction. The anion binding experiments revealed interesting difference in the binding mode: The *cis*-**1** isomer binds anions in a mixed binding mode featuring a combination of hydrogen bonding and anion−π interactions resulting in an unexpected strong binding. On the other hand, the *trans*-**1** isomer displays only hydrogen bonding and lower affinity for anions. This is unexpected as one would assume both isomers to display the same binding modes. Overall, the titrations of **1** using UV spectrophotometry and NMR titrations by anions reveal that *cis*-isomer **1** displays higher affinity (10^5−10^6 M^{-1}) and cross-reactivity for anions, while the *trans*-isomer **1** shows a more selective response to anions. Such differences in binding mode in configurational isomers are so far unexplored and a feature deserving further study.



INTRODUCTION

Anions play important roles in medicine, natural and industrial processes, and biological systems, and the development of artificial anion receptors garnered significant attention.[1] To date, various supramolecular receptors were realized, including Lewis acid[2] or metal coordination,[3] hydrogen bonding,[4] anion−π electron interaction,[5] electrostatic interactions,[6] halogen bonding,[7] and others. Typical hydrogen-bonding based receptors for anions employ thiourea,[8] imidazole/triazole,[9] or amide[10] moieties. Recently, octamethylcalix[4]pyrrole (OMCP), first synthesized by Baeyer in 1886,[11] was rediscovered by Sessler and co-workers as a powerful receptor for anions.[12] Since then, anion receptors based on OMCP have been widely researched and used as a structural platform for preparation of anion sensors.[13] Attachment of functional groups to OMCP is usually carried out at the β-CH position[14,15] or *meso*-position.[16] Particularly β-CH substitution offers marked opportunities for sensor development.[15] On the other hand the *meso*-substitution was used to develop cavity systems,[17] cryptands,[18] capsule,[19] strapped calix[4]pyrroles,[20] and calix[4]pyrroles with pendant arms.[21] In addition, the chemistry of calixpyrroles has been extended for expanded analogues.[22] In spite of the number of studies of calix[4]-pyrroles, the attachment of pyrrole rings to *meso*-positions of OMCP and corresponding anion recognition properties were not fully investigated.[23] To achieve enhanced anion affinity of the OMCP receptor we decided to synthesize a hexapyrrolic calix[4]pyrrole possessing two pyrrole side-arms above or above and below the parent OMCP-macrocycle hoping the NH- moieties of the pyrrole side-arms are able to form a hydrogen bond to a bound anion. Furthermore, the pyrrole side-arms have a carboxyl ester in their 2-positions enabling an attachment of various dyes for sensing applications.[24] Likewise, the compounds **1** retain free β-CH positions for a conversion to sensors. Thus, these derivatives offer an example opportunity as building blocks for molecular devices, particularly capsules utilizing the pyrrole side-arms and sensors based on the β-CH substitution.[15c−g]

RESULTS AND DISCUSSION

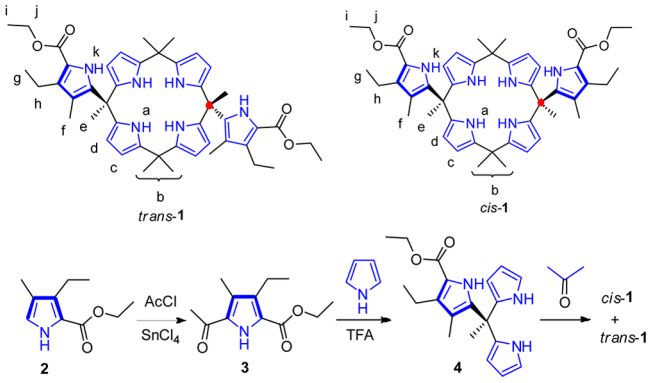
The synthesis of *cis*- and *trans*-**1** was performed using the following methods: 2-ethoxycarbonyl-3-ethyl-4-methyl pyrrole **2** is available through Barton−Zard synthesis.[25] Ethyl 5-acetyl-3-ethyl-4-methyl-1*H*-pyrrole-2-carboxylate **3** was synthesized according to the literature.[26] The compound **3** was condensed with freshly distilled pyrrole in dichloromethane, which afforded ethyl 5-[1,1-bis(1*H*-pyrrol-2-yl)ethyl]-3-ethyl-4-methyl-1*H*-pyrrole-2-carboxylate **4** in 58% yield. Subsequently, the condensation of **4** with acetone in acetonitrile using trifluoroacetic acid gave the desired hexapyrrolic calix[4]pyrrole (**1**) as a mixture of two configurational isomers. These isomers (*cis* and *trans*) differ in the orientation of the *meso*-pyrrole side group with regard to the plane of the calix[4]pyrrole macrocycle. The mixture of isomers was purified by column chromatography on silica, affording pure *cis*- and *trans*-**1** (Scheme 1) with an overall yield of ∼10%.

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Scheme 1. Molecular Structure of 1



The structures of tripyrrole **4** and both isomers **1** were confirmed by NMR spectroscopy, mass spectrometry, and X-ray diffraction analysis. Figure 1 shows the X-ray structures of **4**, while Figure 2 shows the structures of receptors **1**.

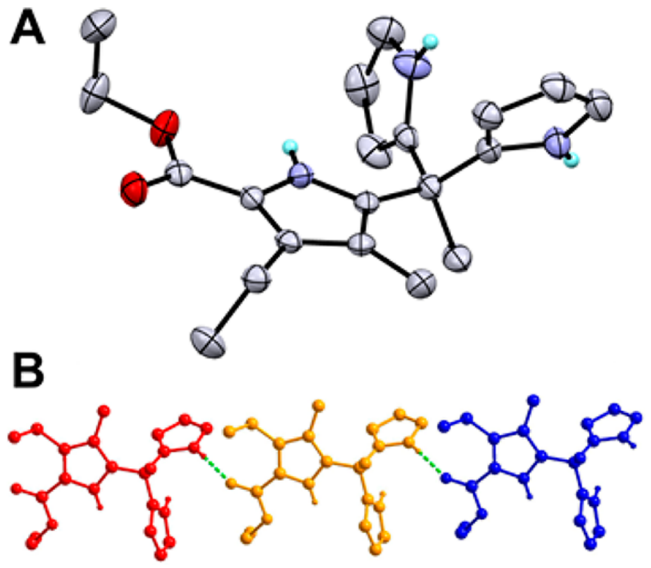


Figure 1. (A) X-ray diffraction analysis of **4**. (B) The X-ray analysis reveals an intermolecular hydrogen bond between pyrrole NH and acyl oxygen in the solid state. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms bound to carbon atoms are omitted. The carbon atoms are shown in gray, the nitrogen in light blue, the oxygen in red, and the hydrogen atoms in aqua blue.

The crystal structures of **1** confirm the assignment of the *cis*- and *trans*-orientation of the *meso*-pyrrole substituents with respect to the calix[4]pyrrole macrocycle. Here, *cis*-**1** displays a 1,3-alternate conformation[27] (Figure 2A), while *trans*-**1** shows a 1,2-alternate conformation[27] (Figure 2B). Recently, Panda et al. reported *cis*- and *trans-meso*-diacylated calix[4]pyrrole to form intermolecular hydrogen-bonded networks.[28] However, *cis*- and *trans*-**1** do not exhibit similar behavior either in the solid state or in the solution as confirmed by ^{1}H NMR experiments with varying concentration of **1** in acetonitrile-d_3 (see the SI).

To clarify the anion binding stoichiometry of **1**, three types of experiments were performed: gas-phase experiments using electrospray ionization (ESI) mass spectrometry, in solution using UV spectroscopy, and by molecular modeling using DFT method for geometry optimization in acetonitrile. ESI-MS experiments: The acetonitrile solution of *cis*-**1** or *trans*-**1** (2.0×10^{-4} M) was mixed with anions (1.0×10^{-3} M) such as fluoride, chloride, acetate, dihydrogen phosphate, hydrogen pyrophosphate, and benzoate. The selection of anions was made to gain an insight into the binding of biologically more relevant anions, phosphates, and carboxylates. The negative mode ESI MS revealed that both isomers of **1** bind anions with 1:1 stoichiometry. The MS data of **1**·anion complexes are summarized in the SI. An example of ESI MS suggesting a strong complexation between *cis*-**1** and benzoate is shown in Figure 3.

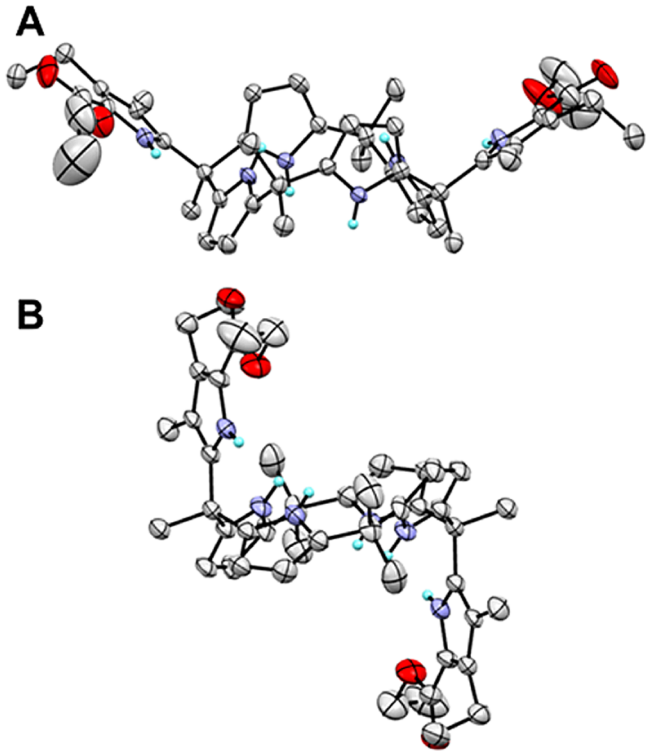


Figure 2. X-ray structures of (A) *cis*-**1** and (B) *trans*-**1**; *cis*-**1** adopts 1,3-alternate conformation, while *trans*-**1** adopts 1,2-alternate conformation. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms bound to carbon atoms are omitted.

Because the absorption of the parent OMCP macrocycle generally occurs in the deep UV region, the investigation of binding affinity for anions is generally carried out by NMR and ITC. Here, however, the hexapyrrolic calix[4]pyrrole **1** possesses pyrrole side-arms that absorb light in the near-UV. This allows performing anion titrations using a UV spectros-

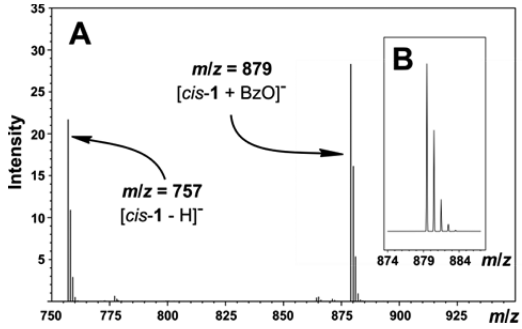


Figure 3. (A) ESI MS spectrum of *cis*-**1**·BzO^- complex. The spectrum showed 1:1 binding stoichiometry. (B) Calculated isotope pattern for $C_{53}H_{63}N_6O_6^-$.

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copy. Figure 4 shows UV spectra of both isomers **1** upon the addition of fluoride in acetonitrile. Both isomers exhibited a

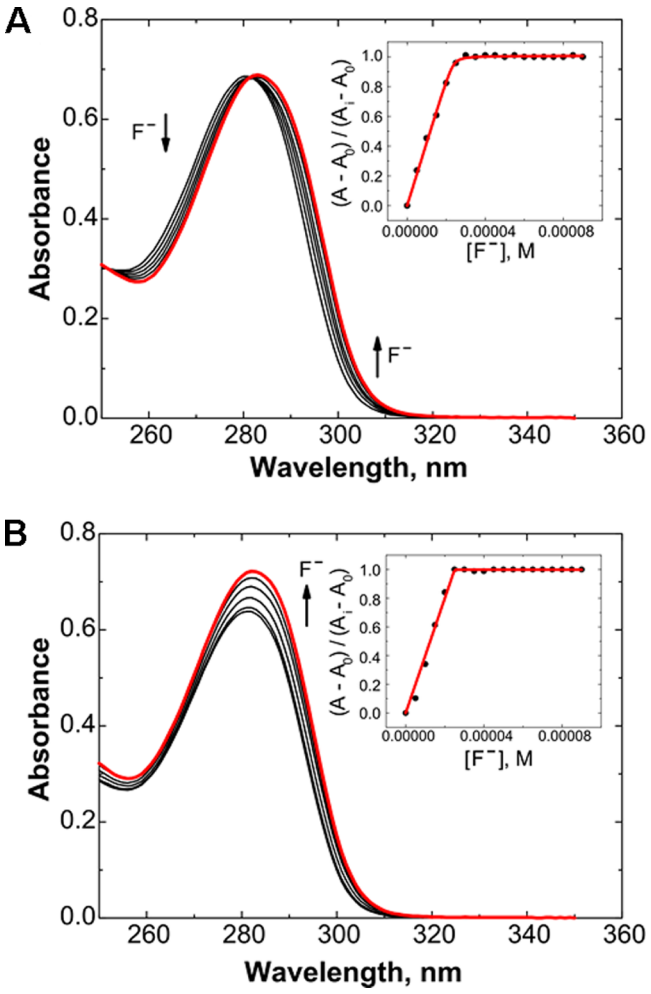


Figure 4. Absorption spectra of **1** (A: *cis*-**1**, B: *trans*-**1**) upon the addition of tetrabutylammonium fluoride in MeCN at rt, [fluoride] = 0−90 μM.

small bathochromic shift (1−5 nm) of spectra upon fluoride addition, suggesting that the side-pyrrole of both isomers interacts with fluoride. However, spectral changes are clearly different between *cis*- and *trans*-**1** (Figure 4A,B), suggesting that the binding mode of *cis*-**1** is different from that of *trans*-**1**.

The binding affinities of *cis*- and *trans*-**1** for various anions are summarized in the Table 1. Overall, the binding constants of both isomers **1** are higher than that of OMCP,[12,29] which lacks side-arm pyrrole assisting in anion binding. As expected, the

Table 1. Binding Constants (K_a, M^{-1}) of 1 for Anions in MeCN[a]

anion	*cis*-**1**	*trans*-**1**
F^-	>1 000 000	>1 000 000
Cl^-	220 000	1900
AcO^-	>1 000 000	200 000
BzO^-	540 000	4300
H_2Pi^-	45 000	7700
$HPPi^{3-}$	23 000	ND

[a]All errors are <17%. ND: biphasic nature of the isotherm.

affinity of *cis*-**1** for anions is stronger than that of *trans*-**1**, particularly in the case of chloride (116 times difference), dihydrogen phosphate (6 times), and benzoate (126 times). The *cis*-**1** binds anions more efficiently than *trans*-**1**; the receptor *cis*-**1** generally shows binding constants K_{as} exceeding 10^4 M^{-1} as well as a high cross-reactivity.[30] On the other hand, *trans*-**1** exhibits lower binding constants and higher selectivity. This increased selectivity is attributed to the high directionality of the hydrogen bonds. The relatively large affinity of **1** for carboxylate derivatives suggests that the compound **1** would be suitable as a building block for sensors for carboxylates such as nonsteroidal anti-inflammatory drugs (NSAIDs).[15c−e]

To investigate the role of pyrrole side-arms in anion binding, ^{1}H NMR titrations of anions were conducted with both isomers **1**. Figure 5A shows ^{1}H NMR spectra of *cis*-**1** upon the addition of fluoride. The assignments of each signal were achieved using 2D NMR (see SI). In these titrations, coupling between calix[4]pyrrole NHs of *cis*-**1** and the bound fluoride was observed. Both calix[4]pyrrole NHs (H_a) and side-arm pyrrole NHs (H_k) show slow exchange kinetics.

To gain further understanding of the recognition process, we have measured 2D NOESY NMR of *cis*-**1** in the absence (Figure 5C) or presence of fluoride (Figure 5D). Figure 5D shows new correlation signals between side-arm pyrrole NHs and CH_3 signals (H_b and H_e). Because *cis*-**1** is fixed in the cone conformation by fluoride, the side-arm pyrrole NHs and CH_3 become close to each other (<5 Å). The downfield shift of the calix[4]pyrrole NHs of *cis*-**1** upon the addition of anions follows the order: fluoride (12.8 ppm) > benzoate (11.8 ppm) ≈ dihydrogen phosphate (11.8 ppm) ≥ acetate (11.7 ppm) ≈ hydrogen pyrophosphate (11.7 ppm) ≥ chloride (11.4 ppm) from the original 8.0 ppm. Figure 5A shows that the calix[4]pyrrole NH resonances undergo a dramatic downfield shift from 8.0 to 12.8 ppm and an upfield shift of the calix[4]pyrrole β-CH signals. The respective coupling constant is 41 Hz.[31] This suggests that calix[4]pyrrole NHs interact with fluoride through a hydrogen bond. However, the pyrrole NH protons on the side-arm (H_k) do not undergo an appreciable downfield shift upon the addition of fluoride. Interestingly, this behavior is consistent with an anion−π interaction.[32] This suggests an anion−π interaction between these pyrrole rings and the bound fluoride rather than hydrogen bonding.[33]

^{1}H NMR titration of *trans*-**1** by fluoride also revealed a fixed cone conformation. In the case of the *trans*-**1** each side-arm resonance is split into two sets of signals (Figure 5B). One of the pyrrole side-arms NH (H_k) shows a significant downfield chemical shift in comparison with *cis*-**1** suggesting a hydrogen bonding between the side-arm pyrrole NH (H_k) and the bound fluoride. The other side-arm NH ($H_{k'}$) shows almost no change of chemical shifts upon the addition of fluoride suggesting that one side-arm pyrrole does not participate in fluoride binding presumably because it is below the plane of the calix[4]pyrrole. Thus, the split signals arise from the nonparticipating side-arm and the resulting loss in symmetry of the host−guest conformation.[34] The downfield shifts of the calix[4]pyrrole NHs of *trans*-**1** upon the addition of anions have the following order: fluoride (12.8 ppm) > benzoate (11.4 ppm) ≈ acetate (11.4 ppm) ≥ chloride (11.1 ppm) > dihydrogen phosphate (10.3 ppm) ≥ hydrogen pyrophosphate (9.9 ppm) from the original 8.1 ppm.

We calculated the energy-minimized structure of the complex of **1** and fluoride in acetonitrile using a DFT method. Figure 6A shows the energy-minimized geometry of the *cis*-**1**·fluoride

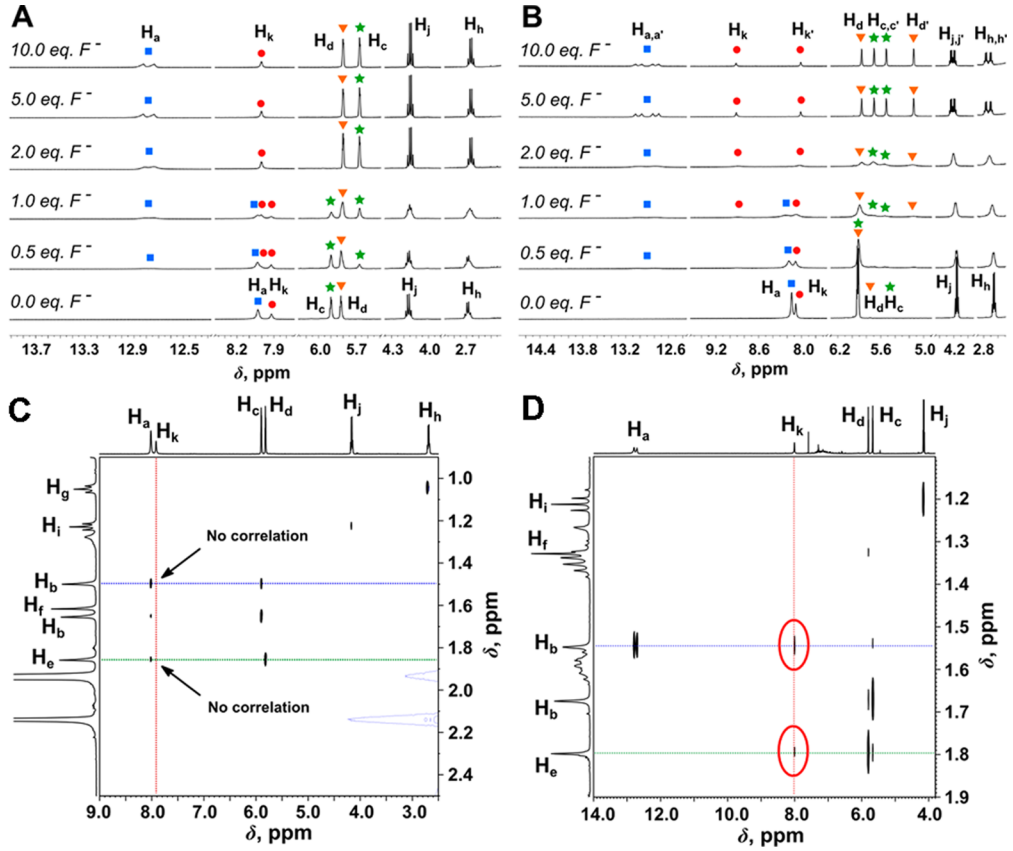


Figure 5. ^{1}H NMR (500 MHz) titration of **1** (A: *cis*-**1**, B: and *trans*-**1**) upon the addition of fluoride. (C) 2D NOESY NMR spectrum of *cis*-**1** without fluoride recorded in CD_3CN. (D) 2D NOESY NMR spectrum of *cis*-**1** with fluoride recorded in CD_3CN.

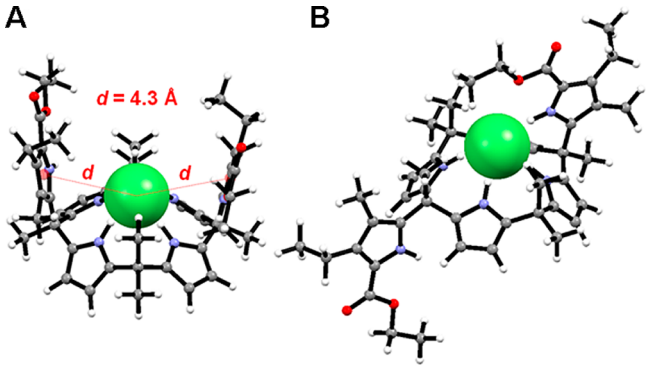


Figure 6. Energy minimized geometry (DFT, B3LYP/6-31G* level) of the complex of (A) *cis*-**1** and (B) *trans*-**1** with fluoride in acetonitrile (fluoride is shown in CPK mode).

complex with both of the calix[4]pyrrole NHs binding fluoride. The calculated model predicts the side-arm pyrrole to interact with fluoride through anion−π interaction. The distances between the centroid of the side-arm pyrrole ring and the fluoride are ∼4.3 Å, which is rather long[35] but still in agreement with previously reported anion−π interactions between anions and *meso*-tetraaryl calix[4]pyrroles.[32] Furthermore, the distance of the side-arm pyrrole NHs and CH_3 (H_b and H_e) is <5 Å, which is in good agreement with the 2D NOESY NMR results (vide supra). The complex of *trans*-**1** with fluoride shows that one of the side-arm pyrrole binds fluoride through hydrogen bonding, while the other side-arm does not bind the guest (Figure 6B), a presumed reason for overall lower affinity for anions compared to *cis*-**1**. This result is also in agreement with the NMR data in Figure 5B.

Finally, the anion binding modes have been confirmed by a DFT study aimed at interpretation of shifts in the NMR spectra corresponding to the energy-minimized model for **1** in the resting state and in the complex with fluoride. Here we show the DFT-GIAO magnetic shielding calculated for **1** and **1**·F^- in their energy minima (Figures 7). The calculation shows the same trend (shifts of the ^{1}H-resonances) as observed during the titration experiments of **1** with fluoride observed for **1** with fluoride in acetonitrile-d_3 (see Figure 5).

The different anion-binding modes in *cis*-**1** and *trans*-**1** are surprising. Naturally, one would expect that the *trans*-**1** isomer would, similarly to *cis*-**1** bind anions in a mixed mode of hydrogen bonding and anion−π interaction, albeit with only one pyrrole side-arm. In fact this is not observed.

■ CONCLUSIONS

In summary, the configurational isomers of a new hexapyrrolic calix[4]pyrrole **1** have been synthesized, and their structure unambiguously characterized by X-ray crystallography. The binding stoichiometry of **1** and anions was investigated by MS, NMR, and UV spectroscopy. Despite the structural similarity, both receptors display different physical interactions to form anion-receptor complex. In the case of the *cis*-**1** isomer the UV titration, NMR analysis, and computational DFT model reveal that the pyrrole side-arms contribute to anion binding by 2-fold anion−π interactions. In contradistinction, the *trans*-**1** isomer forms the receptor-anion complex based solely on hydrogen bonding, i.e., without any contribution from anion−π

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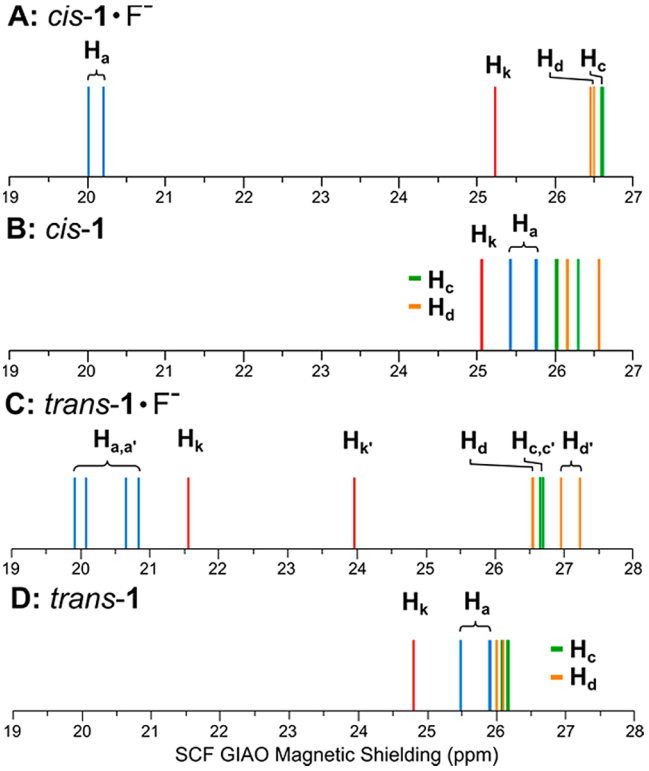


Figure 7. Calculated DFT-GIAO magnetic shielding for **1** (B: *cis*-**1**, D: *trans*-**1**) and **1** with fluoride in 1:1 binding mode (A: *cis*-**1**, C: *trans*-**1**) in acetonitrile at the B3LYP/6-31G* level of theory.

interactions. This is, to the best of our knowledge, the first example of two configurational isomers displaying different binding mode in anion binding. Importantly, the difference in the anion binding modes is reflected directly in the anion-binding affinities by *cis*- and *trans*-**1**. Here, the *cis*-**1** isomer featuring anion−π interactions shows a significant cross-reactivity toward anions, while the *trans* isomer **1** shows more selective response to anions, namely acetate and, to a lesser extent, also fluoride. For the design of sensor arrays, particularly the minimum-sized arrays, it is important to include both selective and cross-reactive probes. Here, isomers of the hexapyrrolic calix[4]pyrrole **1** could offer a good platform for anion sensor arrays. We believe that this study opens up new avenues for the application of calix[4]pyrrole receptors in anion sensing and could aid in the development of a simple array sensor utilizing the free β-CH positions.[15]

■ ASSOCIATED CONTENT

Supporting Information

The details of synthesis and characterisation of compounds **1** and **4**, X-ray data, UV absorption, MS, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

pavel@bgsu.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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