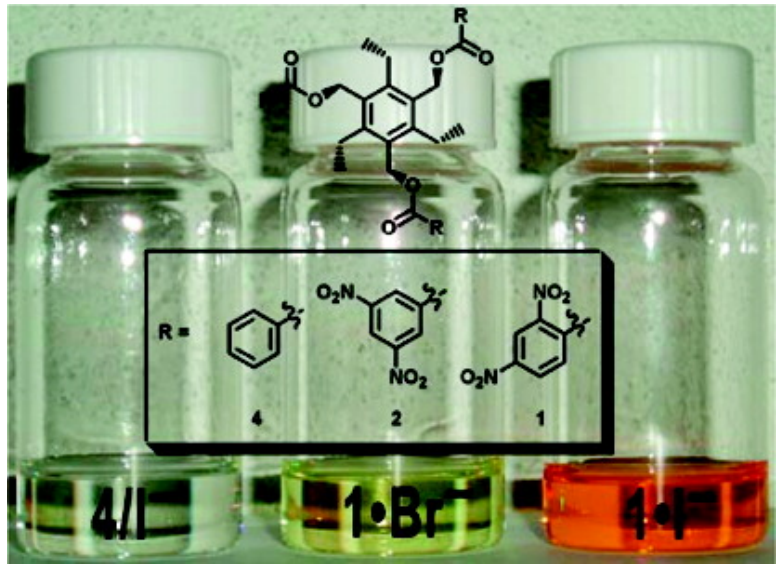
Communication

Solution Phase Measurement of Both Weak # and C#H···X Hydrogen Bonding Interactions in Synthetic Anion Receptors

Orion B. Berryman, Aaron C. Sather, Benjamin P. Hay, Jeffrey S. Meisner, and Darren W. Johnson

J. Am. Chem. Soc., **2008**, 130 (33), 10895-10897 • DOI: 10.1021/ja8035652 • Publication Date (Web): 29 July 2008



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

J|A|C|S
COMMUNICATIONS

Published on Web 07/29/2008

Solution Phase Measurement of Both Weak σ and C−H···X$^-$ Hydrogen Bonding Interactions in Synthetic Anion Receptors

Orion B. Berryman,[†] Aaron C. Sather,[†] Benjamin P. Hay,[‡] Jeffrey S. Meisner,[†] and Darren W. Johnson*,[†]

Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403-1253, and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830-6119

Received May 21, 2008; E-mail: dwj@uoregon.edu

Electron-deficient arenes offer a variety of interaction motifs complementing traditional anion binding strategies. We have shown that at least three distinct binding motifs are possible.[1,2] These motifs, illustrated for Cl$^-$ complexes with 1,2,4,5-tetracyanobenzene (TCB) are (i) the centered, noncovalent anion−π interaction (**A**), (ii) off-center or "weak σ" interactions (**B** and **C**), and (iii) C−H···X$^-$ hydrogen bonds (when acidic H's are available, **D**) (Figure 1). Although much recent attention has focused on the electrostatic anion−π interaction,[3] there is evidence to suggest that this is not the predominant binding mode for many highly electron-deficient arenes.[2] In prior work, we found that strongly electron-deficient arenes, including TCB, exhibit stable weak σ and H-bonded geometries **B**−**D**, whereas the anion−π motif, **A**, was not a stable form in the solid and gas phases.

The majority of prior computational studies on anion−arene interactions have been representative of the molecules in the gas phase. When moving from *silico* to solution, other factors need to be considered;[4–6] therefore, solution phase association constants (K_a) must be measured to understand fully the selectivity that will emerge in binding anions with electron-deficient arenes. In one case K_a's have been determined for model electron-deficient aromatic rings from UV−vis titrations with halides.[7] NMR spectroscopy can provide complementary structural information that is not obtainable with UV−vis spectroscopy. A handful of examples use ^{1}H NMR spectroscopy to characterize anion interactions with electron-deficient aromatic rings in solution, but in many cases, additional attractive interactions are present (such as π-stacking, ion pairing, or hydrogen bonding).[8]

We present experimental and theoretical results on a series of *neutral* tripodal receptors that utilize *only* electron-deficient arenes to bind halides in solution (Figure 2). These receptors employ steric gearing to preorganize electron-deficient arenes, and ^{1}H NMR spectroscopic titrations and DFT calculations confirm that receptors **1**−**3** bind anions in a 1:1 stoichiometry (Table 1 and Figure 3).[9] These studies highlight the first designed receptor to quantitatively measure weak σ contacts between anions and arenes utilizing only electron-deficient aromatic rings.

Three key findings that have not been observed previously for anions interacting with electron-deficient arenes in solution are emphasized: (i) ^{1}H NMR spectroscopy provides sensitive data for determining both the magnitude of anion binding (K_a) and the structure (π contacts vs hydrogen bonding), even for weak binding; (ii) this represents the first observation of receptors binding anions in solution using only electron-deficient aromatic rings with *either* weak σ *or* C−H···X$^-$ hydrogen bonding interactions;[10] and (iii) these data provide the first quantitative comparison of the *relative* stabilities for such interactions in solution.

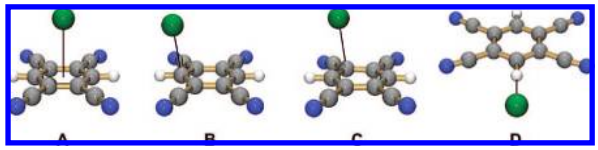


Figure 1. MP2/aug-cc-pVDZ optimized geometries for Cl$^-$ interactions with 1,2,4,5-tetracyanobenzene include an unstable anion−π complex (**A**), weak σ complexes (**B** and **C**), and an aryl H-bond complex (**D**).[1] Atom colors: carbon gray, hydrogen white, nitrogen blue, and chloride green.

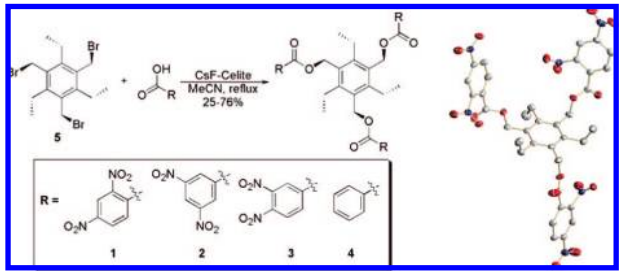


Figure 2. Synthesis of tripodal anion receptors **1**−**3** (left) and ORTEP representation of the crystal structure of receptor **1** (right, 50% probability with hydrogens removed, carbon depicted as gray, hydrogen white, nitrogen blue, and oxygen red).

Table 1. Average[a] K_a (M^{-1}) for Receptors **1**, **2**, and **4**[b] with Halides

	Cl$^-$ [c]	Br$^-$ [c]	I$^-$ [c]
1	26	18	11
2	53	35	26
4	<1[d]	<1[d]	<1[d]

[a] Average K_a reported from 2 to 3 titration experiments (not including receptor **4**). [b] All titrations were performed in C_6D_6 with receptor concentrations of ~2 mM; errors are estimated at ±10%. A titration of receptor **3** and $NBu_4^+Br^-$ in C_6D_6 (with slight heat to increase solubility) yielded a K_a = 12 M^{-1}. [c] Tetra-*n*-heptylammonium halides were used as the salt sources for each experiment, and titrations were performed at 27 °C. [d] $\Delta\delta$ for control receptor **4** were too small to determine K_a's.

The cavity present in *syn* conformers of 2,4,6-trisubstituted 1,3,5-triethylbenzene[11] derivatives provides access for monatomic anions to interact with the electron-deficient dinitroarenes via the π-system or hydrogen bonding (Figure 2). Receptors **1**−**3** are structural isomers composed of three electron-deficient arenes differing only in the position of their nitro substituents, which allows for an understanding of the effect of substitution pattern on receptor function. A key feature of the design strategy is that receptor **2** cannot form hydrogen bonds to anions (due to the bulky nitro groups being positioned *ortho* to each acidic aryl hydrogen), allowing us to study only the interaction between

[†] University of Oregon.
[‡] Oak Ridge National Laboratory.

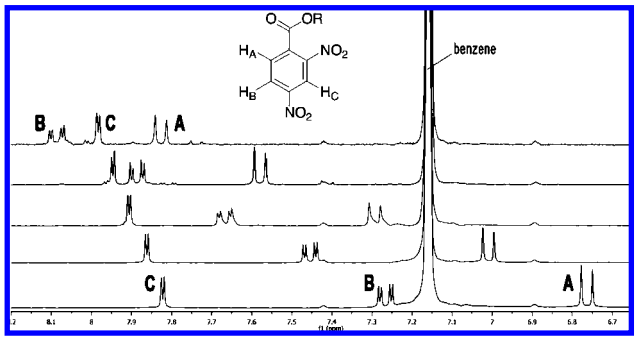


Figure 3. ^{1}H NMR spectra from titrations of receptor **1** (4.95 mM) with $NBu_4^+Br^-$ highlighting the chemical shift changes for this system. The ^{1}H NMR spectrum of **1** is compared to spectra of **1** in the presence of 7, 31, 51, and 101 equiv of $NBu_4^+Br^-$ in ascending order.

the anion and the π-system. Receptor **4**, lacking electron-deficient arenes, was also prepared as a control.

Receptors **1**−**4** were synthesized in good yields from CsF−Celite-assisted esterification of known 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene **5** with the corresponding benzoic acids (Figure 2, Supporting Information).[12] Interestingly, the structures determined from colorless single crystals of **1** and **2** (Supporting Information)[13,14] reveal they crystallize with one electron-deficient ring *anti* with respect to the other arenes (Figure 2). Nevertheless, receptors **1**−**4** exhibit time-averaged C_{3v} symmetry in solution on the NMR time scale, suggesting that the up, up, down conformation does not dominate in solution.

A previous study of strongly electron-deficient aromatic rings illustrated that UV−vis spectroscopy is a suitable method to determine association constants for weak attractive interactions between halides and electron-deficient aromatic rings.[7,15] We chose to investigate the utility of ^{1}H NMR spectroscopy to determine association constants between halides (Cl^-, Br^-, and I^-) and electron-deficient arenes in benzene, in part for the additional structural information provided by this technique. It is necessary when performing titration experiments to obtain data where there is maximal change in the binding isotherm.[16] For solubility reasons, it was challenging to find an organic solvent where subtle interactions could be measured and the anion concentration could reach a large excess of the receptor concentration. The low solubility of $NBu_4^+I^-$ and $NBu_4^+Cl^-$ in C_6D_6 prompted us to perform titration experiments with tetra-*n*-heptylammonium halide salts ($NHep_4^+Cl^-$, $NHep_4^+Br^-$, and $NHep_4^+I^-$) at 27 °C. All three electron-deficient receptors **1**−**3** turned pale yellow upon addition of Br^- (see Table of Contents graphic, middle, picture exemplifies 90 equiv of tetra-*n*-butylammonium bromide, $NBu_4^+Br^-$). Whereas **2** showed relatively little change in the ^{1}H NMR spectrum, *significant* changes occurred with receptors **1** *and* **3** when $NHep_4^+Br^-$ was titrated into C_6D_6 solution of receptors (**3** was poorly soluble which prevented acquiring quantitative data). Association constants determined for receptors **1** and **2** measured 18−35 M^{-1},[17] while control receptor **4**—distinctly lacking electron-deficient arenes—exhibited no measurable binding by NMR and no visible color change (Table 1). These results lend support to our hypothesis that electron-deficient aromatic rings are required to bind anions in this neutral system.

Titrations of receptors **1** and **3** with $NBu_4^+Br^-$ displayed changes in chemical shifts of over 1 ppm,[18] and in the case of receptor **1** with $NBu_4^+Br^-$, the peak juxtaposition even changed over the course of the titrations (Figure 3).[10] Conversely, 3,5-dinitro-substituted receptor **2** exhibited much smaller chemical shift changes (maximum of 0.038 ppm for $NHep_4^+Br^-$), but binding constants were determined to be on the same order of magnitude. The striking differences in $\Delta\delta$ for receptors **1** and **3** versus that for receptor **2** indicate that different binding modes are occurring in solution for these receptors.

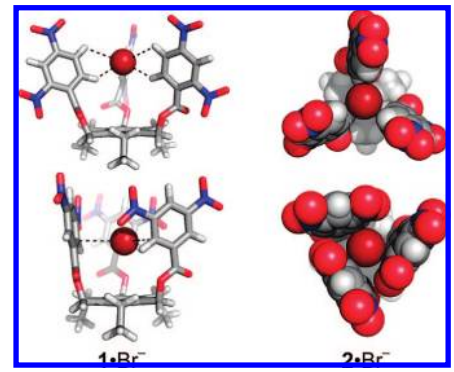


Figure 4. Optimized geometries (B3LYP/DZVP) comparing the aryl C−H hydrogen bonding mode of **1** (top) with the weak σ binding mode of **2** (bottom). Atom colors: carbon gray, hydrogen white, nitrogen blue, oxygen red, and bromine rust.

Further evidence for the identity of these binding modes is provided by DFT calculations.[19] B3LYP/DZVP calculations were performed on 1:1 complexes between Br^- and single arenes from **1** and **2** that possess the same substitution patterns but with methyl ester substituents (Figure S2, Supporting Information). Interestingly, optimizations starting from an idealized anion−π geometry, with the Br^- anion located directly over the arene centroid at a distance of 3.2 Å,[2] in both cases failed to yield the expected anion−π complex. Rather, the model corresponding to **1** gave a H-bonded form ($\Delta E = -20.7$ kcal/mol)[20,21] and that of **2** gave a weak σ complex, with the Br^- located above a carbon atom *ortho* to the ester substituent ($\Delta E = -19.7$ kcal/mol). This behavior, consistent with that exhibited by other highly electron-deficient arenes,[1,2] suggests that the anion−π interaction is not a preferred binding motif for the arene acceptors in **1** and **2**.

The calculations of the model complexes forecast the results of calculations on Br^- complexes of **1** and **2**. Geometries for these complexes, confirmed to be minima by frequency calculations (Figure 4), are fully consistent with the NMR evidence. In **1**, Br^- forms bifurcated H-bonds to each arene, with H···Br^- distances of 2.72 Å (H_A, Figure 3) and 3.18 Å (H_B, Figure 3). In agreement with the spectra, the shortest hydrogen bonding interaction yields the largest chemical shift.[22] In **2**, where H-bonding to the arene is not possible due to steric repulsions, Br^- binds to the arenes via weak σ interactions, with distances of 3.31 Å to the nearest carbon atom in each arene. Lacking direct interaction with aryl hydrogen atoms, this binding motif is consistent with the small chemical shifts observed in the ^{1}H NMR spectrum for **2**•Br^-.

Further solution studies, conducted with $NHep_4^+Cl^-$ and $NHep_4^+I^-$ (Supporting Information), yield results that further support conclusions obtained from the Br^- studies. Whereas the **1**•Cl^- complex is colorless in C_6D_6, the **2**•Cl^- complex presents a pale yellow color in solution. An orange color change was observed for all receptors **1**−**3** with $NHep_4^+I^-$ (Table of Contents graphic, right, demonstrates the color observed when 84 equiv of $NHep_4^+I^-$ are present at 27 °C).[23] Analogous to the Br^- titration experiments in C_6D_6, significantly larger chemical shift changes were observed for **1** over those of **2**, again consistent with the fact that **1** can form aryl CH···X^- H-bonds while **2** cannot. Titrations of **1** and **2** with $NHep_4^+Cl^-$ exhibited the largest K_a values (ranging from 26 to 53 M^{-1}, Table 1). For I^-, ^{1}H NMR titrations at 27 °C reveal association constants ranging from 11 to 26 M^{-1}. As with Br^-, control receptor **4** fails to form colored complexes with Cl^- or I^- and exhibits no measurable association in C_6D_6.

Through a series of receptors utilizing only electron-deficient arenes to bind anions, we have shown that ^{1}H NMR spectroscopy is a practical means to measure these subtle interactions in solution. DFT calculations and ^{1}H NMR titrations establish that the nitro group substitution pattern

is critical to the binding mode adopted by the receptor. The 2,4- and 3,4-substitution patterns in **1** and **3** engender the interaction with anions through aryl C−H···X$^-$ hydrogen bonding, while the 3,5-substitution pattern in **2** promotes weak σ interactions. With two NO_2 and one ester substituent, these highly electron-deficient arenes adopt binding motifs of weak σ and aryl H-bonding instead of the anion−π motif. The differences in binding modes between isomeric receptors **1** and **2** have allowed us to quantify for the first time distinction between aryl H-bonds and anion/arene π contacts, which are in conflict when acidic aryl hydrogens are present. Receptors **1** and **2** exhibit the strongest interactions with Cl$^-$ followed by Br$^-$ and I$^-$, and larger association constants are observed when the halide is restricted to interact solely through contacts to the π-system (receptor **2**). Does this approach hint at an emerging selectivity for anion binding in solution using electron-deficient arenes? Receptors that exhibit larger binding constants with more striking differences will need to be studied to further address this issue.

Acknowledgment. O.B.B. acknowledges the NSF for an Integrative Graduate Education and Research Traineeship (DGE-0549503). J.S.M. recognizes the Ronald E. McNair Program for its support. D.W.J. is a Cottrell Scholar of Research Corporation and gratefully acknowledges the NSF for a CAREER award. Dr. Lev N. Zakharov is acknowledged for assistance with the single-crystal X-ray diffraction experiments. B.P.H. acknowledges support from the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy (DOE) under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory (managed by UT-Battelle, LLC). DFT calculations were performed using the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory managed for DOE by Battelle.

Supporting Information Available: Full experimental details, including synthesis, spectroscopic, titration, and structural details for all compounds described; crystallographic data of **1** and **2** (CCDC #s 661394−661395); details of DFT calculations and relevant references are available. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Berryman, O. B.; Bryantsev, V. S.; Stay, D. P.; Johnson, D. W.; Hay, B. P. *J. Am. Chem. Soc.* **2007**, *129*, 48.

(2) Hay, B. P.; Bryantsev, V. S. *Chem. Commun.* **2008**, 2417.

(3) Weak, reversible attractions between anions and electron-deficient arenes, and putative structures for the different interaction types (including each of the interactions **A**−**D**), have been reported. For representative examples, see: (a) Buncel, E.; Norris, A. R.; Russell, K. E. *Q. Rev. Chem. Soc.* **1968**, *22*, 123. (b) Hiraoka, K.; Mizuse, S. *J. Phys. Chem.* **1987**, *91*, 5294. (c) Kebarle, P.; Chowdhury, S. *Chem. Rev.* **1987**, *87*, 513. Recent computational studies have attracted considerable attention and have attempted to characterize the interaction(s) in greater detail; see: (d) Alkorta, I.; Rozas, I.; Elguero, J. *J. Am. Chem. Soc.* **2002**, *124*, 8593. (e) Mascal, M.; Armstrong, A.; Bartberger, M. D. *J. Am. Chem. Soc.* **2002**, *124*, 6274. (f) Quinonero, D.; Garau, C.; Rotger, C.; Frontera, A.; Ballester, P.; Costa, A.; Deya, P. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3389. For additional recent reviews, see: (g) Gamez, P.; Mooibroek, T. J.; Teat, S. J.; Reedijk, J. *Acc. Chem. Res.* **2007**, *40*, 435. (h) Schottel, B. L.; Chifotides, H. T.; Dunbar, K. R. *Chem. Soc. Rev.* **2008**, *37*, 68.

(4) Bianchi, A., Bowman-James, K., Garcia-Espana, E., Eds. *Supramolecular Chemistry of Anions*; Wiley-VCH: New York, 1997.

(5) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry*; The Royal Society of Chemistry: Cambridge, UK, 2006.

(6) Sessler, J. L.; Gross, D. E.; Cho, W.-S.; Lynch, V. M.; Schmidtchen, F. P.; Bates, G. W.; Light, M. E.; Gale, P. A. *J. Am. Chem. Soc.* **2006**, *128*, 12281.

(7) Rosokha, Y. S.; Lindeman, S. V.; Rosokha, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 4650.

(8) For solution examples of anions interacting with electron-deficient arenes, see: (a) Berryman, O. B.; Hof, F.; Hynes, M. J.; Johnson, D. W. *Chem. Commun.* **2006**, 506. (b) Gil-Ramirez, G.; Escudero, E. C.; Benet-Buchholz, B.; Ballester, P. *Angew. Chem., Int. Ed.* **2008**, *44*, 4114. (c) See ref 7. (d) Lakshminarayanan, P. S.; Ravikumar, I.; Suresh, E.; Ghosh, P. *Inorg. Chem.* **2007**, *46*, 4769. (e) Fairchild, R. M.; Holman, K. T. *J. Am. Chem. Soc.* **2005**, *127*, 16364. (f) Maeda, H.; Osuka, A.; Furuta, H. *J. Inclusion Phenom. Macrocycl. Chem.* **2004**, *49*, 33. (g) Gorteau, V.; Bollot, G.; Mareda, J.; Perez-Velasco, A.; Matile, S. *J. Am. Chem. Soc.* **2006**, *128*, 14788. (h) Schneider, H. J.; Werner, F.; Blatter, T. *J. Phys. Org. Chem.* **1993**, *6*, 590. (i) For a recent solid state example, see: Albrecht, M.; Wessel, C.; Groot, M.; Rissanen, K.; Luchow, A. *J. Am. Chem. Soc.* **2008**, *130*, 4600.

(9) Job plots measured at concentrations lower than the dissociation constants involved are inherently unreliable; see: Huang, C. Y.; Zhou, R.; Yang, D. C. H.; Chock, P. B. *Biophys. Chem.* **2003**, *100*, 143. Unfortunately, this system is limited to combined concentrations of ~20 mM. However, fitting the isotherms of all 16 titrations to higher order binding stoichiometries resulted in K^a's that were highly dependent on starting estimates. Furthermore, these fits were not reproducible among experiments run in duplicate or triplicate.

(10) ^{1}H NMR spectroscopy has been used previously to demonstrate C−H···X$^-$ hydrogen bonds in solution; see: (a) Li, Y.; Flood, A. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 2649. (b) Juwarker, H.; Lenhardt, J. M.; Pham, D. M.; Craig, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 3740. For other examples of complementary C−H···X$^-$ hydrogen bonding modes in receptors that bind anions using traditional H-bonds (c−g) or electrostatic attractions (h,i), see: (c) Lee, C.-H.; Na, H.-K.; Yoon, D.-W.; Won, D.-H.; Cho, W.-S.; Lynch, V. M.; Shevchuk, S. V.; Sessler, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 7301. (d) Kwon, J. Y.; Jang, Y. J.; Kim, S. K.; Lee, K.-H.; Kim, J. S.; Yoon, J. *J. Org. Chem.* **2004**, *69*, 5155. (e) Chen, Q.-Y.; Chen, C.-F. *Tetrahedron Lett.* **2004**, *45*, 6493. (f) Ghosh, S.; Choudhury, A. R.; Row, T. N. G.; Maitra, U. *Org. Lett.* **2005**, *7*, 1441. (g) Fujimoto, C.; Kusunose, Y.; Maeda, H. *J. Org. Chem.* **2006**, *71*, 2389. (h) Wallace, K. J.; Belcher, W. J.; Turner, D. R.; Syed, K. F.; Steed, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 9699. (i) Vega, I. E. D.; Gale, P. A.; Light, M. E.; Loeb, S. J. *Chem. Commun.* **2005**, 4913.

(11) Hennrich, G.; Anslyn, E. V. *Chem.—Eur. J.* **2002**, *8*, 2218.

(12) Lee, J. C.; Choi, Y. *Synth. Commun.* **1998**, *28*, 2021.

(13) Crystal data for **1**: $C_{36}H_{30}N_6O_{18}$, M = 834.66, triclinic, $P\bar{1}$, a = 5.6949(12) Å, b = 19.833(4) Å, c = 33.883(7) Å, α = 84.106(4)°, β = 85.278(5)°, γ = 81.873(5)°, V = 3759.6(14) Å^3, Z = 4, μ(Mo Kα) = 0.121 mm^{-1}; $R1$ = 0.0566 (1321 parameters, 16401 reflections with $I > 2\sigma(I)$); $R1$ = 0.1090, $wR2$ = 0.1446, GoF = 1.007 for all 23621 data.

(14) Crystal data for **2**: $(C_{36}H_{30}N_6O_{18})(C_2H_6OS)_3$, M = 1069.04, monoclinic, $P2(1)/n$, a = 28.272(12) Å, b = 5.075(2) Å, c = 37.126(15) Å, β = 110.669(7)°, V = 4984(4) Å^3, Z = 4, μ(Mo Kα) = 0.091 mm^{-1}; $R1$ = 0.0857 (544 parameters, 8731 reflections with $I > 2\sigma(I)$); $R1$ = 0.1736, $wR2$ = 0.2640, GoF = 0.946 for all 33339 data.

(15) UV−vis titrations for **1** and **2** with NHep$_4^+$I$^-$ at 21 °C were performed to corroborate the ^{1}H NMR titrations herein. Regrettably, the charge transfer band that grows in throughout the titration appears as a shoulder on the residual NHep$_4^+$I$^-$ band that increases throughout the titration (see Supporting Information).

(16) Hirose, K. *J. Inclusion Phenom. Macrocycl. Chem.* **2001**, *39*, 193.

(17) Titrations of receptors **1** and **2** (~5 mM) with tetra-*n*-butylammonium bromide (NBu$_4^+$Br$^-$) were performed at room temperature resulting in lower association constants (averaging 4−6 M^{-1}). These data indicate that countercation and/or temperature plays a role in the anion binding ability of this system. Nevertheless, titrations of receptor **1** at these concentrations (~5 mM) better illustrate the dramatic $\Delta\delta$ for this receptor.

(18) Analogous titrations of **1** (2 mM) at 27 °C with NHep$_4^+$ halides also exhibit striking peak movement (up to 0.632 ppm for NHep$_4^+$Cl$^-$, 0.500 ppm for NHep$_4^+$Br$^-$, and 0.390 ppm for NHep$_4^+$I$^-$) throughout the experiment (Table 1 and Supporting Information).

(19) DFT calculations were performed with the NWCHEM program (a) using the B3LYP functional (b−e) with the DZVP basis set and DGauss A1 coulomb fitting (f). (Optimized geometries and absolute energies for all structures are provided as Supporting Information.) (a) Bylaska, W.; *NWChem, A Computational Chemistry Package for Parallel Computers*, version 5.0; Pacific Northwest National Laboratory: Richland, WA, 2006; for a full author list, see Supporting Information. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (c) Becke, A. D. In *The Challenge of d and f Electrons: Theory and Computation*; Salahub, D. R., Zerner, M. C., Eds.; ACS Symposium Series, No. 394; American Chemical Society: Washington, DC, 1989; p 166. (d) Becke, A. D. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 599. (e) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. (f) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

(20) Bryantsev, V. S.; Hay, B. P. *Org. Lett.* **2005**, *7*, 5031.

(21) Bryantsev, V. S.; Hay, B. P. *J. Am. Chem. Soc.* **2005**, *127*, 8282.

(22) An alternate conformation, 6.0 kcal/mol higher in energy, was located for **1**·Br$^-$, where the Br$^-$ forms a weak σ complex (3.432 Å) with one arene and bifurcated aryl H-bonds (2.832, 3.043, 2.909, and 3.021 Å) with the other two (see Supporting Information). It is possible that the H-bond complex and/or the weak σ structure is responsible for the colors observed in solution when receptors **1** and **3** are mixed with Br$^-$ or I$^-$.

(23) As a control, no color is observed when NHep$_4^+$Cl$^-$, NHep$_4$+Br$^-$ or NHep$_4^+$I$^-$ are dissolved in C_6D_6 and heated to 27 °C.

JA8035652