

Anion Binding by Electron-Deficient Arenes Based on Complementary Geometry and Charge Distribution

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 Supporting Information

ABSTRACT: Extended electron-deficient arenes are investigated as potential neutral receptors for polyanions. Anion binds via σ interaction with extended arenes, which are composed solely of C and N ring atoms and CN substituents. As a result, the positive charge on the aromatic C is enhanced, consequently maximizing binding strength. Selectivity is achieved because different charge distributions can be obtained for target anions of a particular geometry. The halides F^- and Cl^- form the most stable complex with **6**, while the linear N_3^- interacts most favorably with **7**. The trigonal NO_3^- and tetrahedral ClO_4^- fit the 3-fold rotational axis of **6** but do not form stable complexes with **5** and **7**. The Y-shaped $HCOO^-$ forms complexes with **4**, **5**, and **7**, with the latter being the most stable. Thus, the anion complexes exhibit strong binding and the best geometrical fit between guest and host, reminiscent of Lego blocks.

INTRODUCTION

Anion recognition chemistry has grown as an important research area since the early 1960s because of the central role of anions in biological and chemical systems and its involvement in environmental pollution. Sensors commonly utilize ionic ($C-H$) $^+ \cdots X^-$ and neutral ($N-H$) $\cdots X^-$ hydrogen-bonding interactions in the detection of anions.^{1,2} On the other hand, the design of neutral anion receptors using Lewis acidic aromatic rings is a relatively recent research field.

Theoretical calculations of anion interaction with arenes in the gas phase show three types: (1) σ interaction, where the anion attacks a partially positive aromatic carbon, in effect changing the hybridization of the latter to sp^3 ; (2) anion- π interaction, primarily involving electrostatic (between the negative charge of the anion and the positive quadrupole moment of the arene) and dispersion effects; and (3) hydrogen-bond interaction arising from the increased acidity of the C-H donor due to electron-withdrawing groups.^{3–6} There is no established delineation between anion- π and weak covalent σ interaction; however, on the basis of extensive studies of mostly halide complexes, Hay et al.^{4b} proposed that the maximum density in the region between anion and arene, ρ_{max} is $<0.012\text{ e } \text{\AA}^{-3}$ for anion- π , $0.012 \leq \rho_{max} \leq 0.100\text{ e } \text{\AA}^{-3}$ for weak σ , and $\rho_{max} > 0.100\text{ e } \text{\AA}^{-3}$ for strong σ interaction. It has been demonstrated that either the σ or the H bond complex is the global minimum conformation for the interaction between anion and Lewis acidic aromatic rings, particularly for F^- complexes. Nevertheless, experimental evidence of anion- π interaction has been reported, the stability of which can be attributed to environmental factors such as solvation and crystal packing effects.^{5c,7} Anion- π interaction has also been found in existing X-ray crystal structures, as discussed in a recent review.⁸

Receptors for polyatomic anions commonly utilize H bond interactions.⁹ It was demonstrated that H bond directionality can be exploited to achieve steric constraints for anion shape

recognition in urea-based host structures.¹⁰ On the other hand, anion recognition based on σ interaction has not been explored as extensively as other modes of interaction. Some experimental results show that this is a promising area of research for the development of an anion receptor. A neutral tripodal receptor composed of dinitroarenes has been reported to bind halides in solution by forming weak σ interactions.¹¹ Anion- σ binding by trinitrobenzene has been subsequently confirmed by an IR spectroscopic assay in the gas phase.¹² Fluoride was also shown to bond covalently to hexafluorobenzene through mass spectrometry.¹³ An attractive feature of the anion- σ interaction is that the resulting charge transfer absorption bands occur in the visible region, enabling colorimetric detection of anions.¹⁴ Possible weak σ interactions have been noted in some cases, as in polyazapyridinophane and hexasubstituted benzene-based receptors for NO_3^- , but have not been confirmed.^{9c,d}

Weak σ interaction, and possibly anion- π interaction, are generally enhanced with increased electron deficiency in the arene,^{3–6} and, as such, extended Lewis acidic arenes are viable receptors to strongly bind larger anions. Moreover, electron-deficient aromatic moieties, such as *N*-heteroaromatic rings, are characterized by nonuniform charge distribution, which can be exploited to specifically target anions of a particular charge distribution and geometry. In the present study, seven single and extended aromatic systems **1**–**7** are considered, composed solely of C and N, to find suitable anion receptors for halides (F^- and Cl^-) and linear (N_3^-), trigonal (NO_3^- , $HCOO^-$), and tetrahedral (ClO_4^-) polyatomic anions (Figure 1). In particular, strong binding was observed for F^- , Cl^- , NO_3^- , and ClO_4^- with **6**, $HCOO^-$ with **4** and **7**, and N_3^- with **7**.

Received: September 20, 2011

Published: November 23, 2011

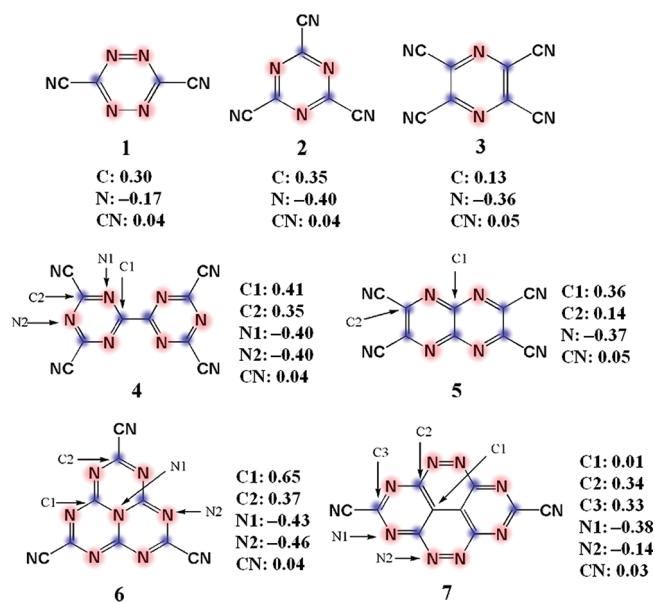


Figure 1. Seven types of arenes have different charge distributions due to the difference in electronegativities between the carbon and nitrogen atoms involved. Natural bond order (NBO) atomic charges of each system are shown in au. The net charge on the CN substituent is 0 au with positively charged C and negatively charged N ($|q(C/N)| = 0.2\text{--}0.3$ au).

CALCULATION METHODS

Ab initio calculations were performed using Gaussian 03.¹⁵ The initial structures were optimized using Moller-Plesset second-order perturbation theory (MP2) with the 6-31+G* basis set and subsequently with the aug-cc-pVDZ (abbreviated as aVDZ) basis set. Frequency calculations were done at the MP2/aVDZ level to confirm minimum energy structures for all anion complexes of **1–5** and halide complexes of **6** and **7**. Because of the computational cost, frequency calculations for **6**-NO₃⁻, **6**-ClO₄⁻, **7**-HCOO⁻, and **7**-N₃⁻ were performed at the MP2/6-31+G* level. The low-lying energy structures were corrected for basis set superposition error (BSSE) using the counterpoise (CP) method of Boys and Bernardi.¹⁶ The MP2/aug-cc-pVTZ (abbreviated as aVTZ) energy was determined to obtain the binding energies at the complete basis set (CBS) limit, which is based on the extrapolation method exploiting the fact that the electron correlation energy is proportional to N^{-3} for the aug-cc-pVNZ basis set.¹⁷ Natural population analysis (NPA) charges, where the charge distribution is derived from the basis functions representing the wave function,¹⁸ were calculated at the MP2/aVDZ level.

RESULTS AND DISCUSSION

A search on the Cambridge Structural Database (CSD, version 5.32 November 2010) revealed that 65 complexes containing arene moieties **1–3** exhibit possible σ interaction with halides at distances $R(X-C) = 3.3\text{--}3.4$ Å. In comparison, H bond interactions were found in 52 complexes at $R(X\cdots H) = 2.7\text{--}2.8$ Å and halide- π interactions in 45 complexes at vertical distance $R_v = 3.4\text{--}3.5$ Å. For interactions between arene moieties and NO₃⁻, 31 complexes in anion- π interactions (and possibly weak σ interactions) were found where the vertical distance between anion centroid and arene plane is $R_v = 3.3\text{--}3.6$ Å and

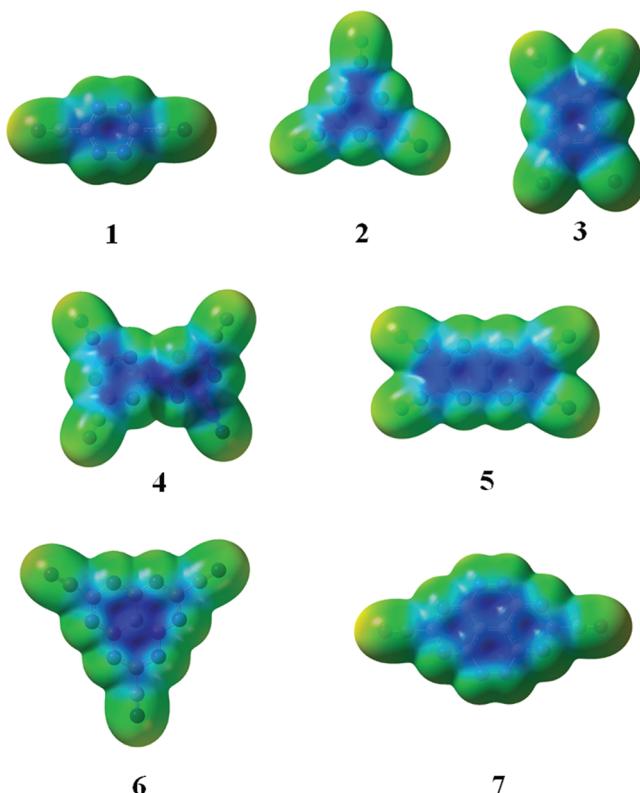


Figure 2. Molecular electrostatic potential (MEP) maps of **1–7**, with the blue regions as positive and red as negative. Density rendered at $0.0020 \text{ e } \text{\AA}^{-3}^{1/2}$ isovales.

the relative orientations of the molecular planes are distributed over 0–90°. In the case of ClO₄⁻, 70 complexes in anion- π interactions (and possibly weak σ interactions) were found where the vertical distance between anion centroid and arene plane is $R_v = 3.7\text{--}3.8$ Å, while most complexes adopt a T-shaped orientation (Supporting Information).

Figure 1 shows the natural bond order (NBO) charge distribution of seven single and extended aromatic systems **1–7**, composed solely of C and N. An electron-withdrawing CN substituent (charge $q = 0$ au) instead of H ($q = 0.2$ au) makes the aromatic core more positive, resulting in enhanced anion binding strength. **1**, **2**, and **3** are single arenes whose aromatic cores are composed of four, three, and two negatively charged N atoms. The atomic charge of the aromatic C of **2** is the most positive ($q = 0.35$ au). **4–7** are extended arenes. In the cases of **4** and **5**, the central aromatic carbons (C1) are highly positive, with $q = 0.41$ and 0.36 au, respectively. **6** has a highly positive carbon C1 ($q = 0.65$ au) surrounded by three N atoms. The central C1's of **7** are surrounded by four positively charged C2's ($q = 0.34$ au). **1–6** are synthesized; **7** is a hypothetical system to bind Y-shaped and linear anions. Figure 2 shows molecular electronic potential (MEP) maps of **1–7**.

Optimized geometries for the anion complexes of single ring and extended systems are shown in Figure 3, with geometric and energetic parameters summarized in Table 1. Data for the other isomers can be found in the Supporting Information. The anion complexes are all true minima. The most stable F⁻ complexes with **1–3** involve strong covalent σ interaction between the aromatic C and F⁻, as evidenced by the significant charge transfer ($q_{CT} \approx 0.5$) (Table 1) and mixing of anion and arene

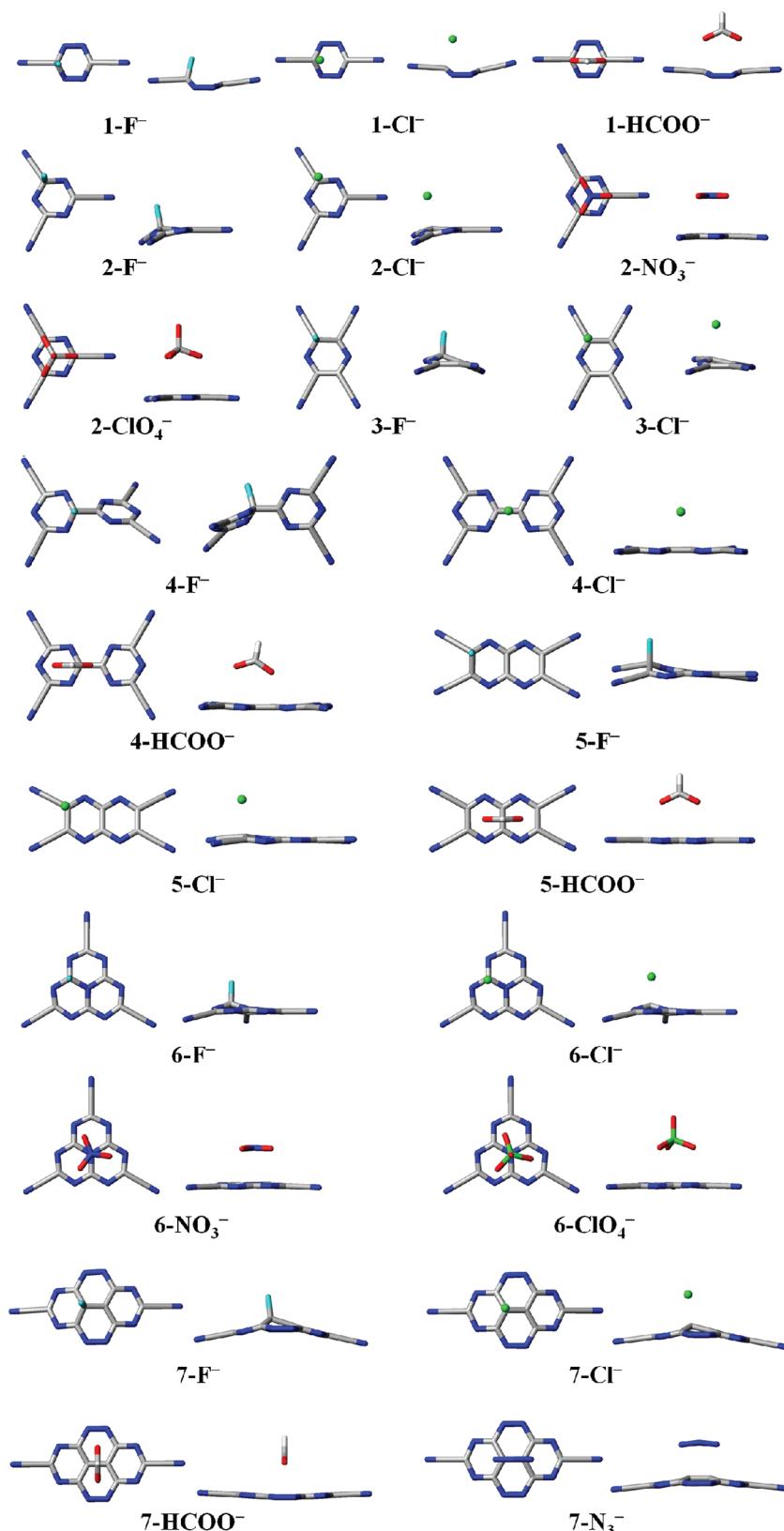


Figure 3. Optimized geometries (top and side views) of anion complexes of **1–7** at the BSSE-corrected MP2/aug-cc-pVDZ level.

orbitals. Bond distances are $\sim 1.5 \text{ \AA}$, and the aromatic C assumes a tetrahedral geometry. **1-F⁻** has the largest binding energy (70.0 kcal/mol), in which the arene has the most positive

N atoms. Covalent σ complexes of **1–3** with Cl⁻ have lower binding energies (35–40 kcal/mol); however, q_{CT} and mixing of orbitals are comparable to those of the F⁻ complexes as shown

in Table 1 and Figure 4. Cl–C distances are longer (2.2–2.4 Å) than the experimental Cl–C(sp³) bond length (1.76 Å).¹⁹

Table 1. BSSE-Corrected MP2/CBS Binding Energies E_{MP2} (kcal/mol), Bond Distance R (Å), and Charge Transfer q_{CT} for the Global Minimum Structures of Anion Complexes of 1–7 in the Gas Phase

complex ^a	R , Å ^b	$-q_{\text{CT}}^c$	E_{MP2} , kcal/mol		
			aVDZ	aVTZ	CBS ^d
1–F [−]	1.49 (C)	0.52	63.25	68.01	70.01
1–Cl [−]	2.24 (C)	0.52	36.16	39.31	40.64
1–HCOO [−]	2.31 (C)	0.20	38.71	40.48	41.22
2–F [−]	1.49 (C)	0.52	63.39	67.89	69.78
2–Cl [−]	2.27 (C)	0.58	32.38	35.10	36.24
2–NO ₃ [−]	2.75 (C)	0.07	28.40	29.67	30.20
2–ClO ₄ [−]	2.80 (C)	0.05	25.89	27.06	27.56
3–F [−]	1.52 (C)	0.52	62.02	66.34	68.16
3–Cl [−]	2.42 (C)	0.40	36.02	38.29	39.24
4–F [−]	1.47 (C1)	0.52	66.34	71.04	73.01
4–Cl [−]	2.60 (C1)	0.30	41.18	43.71	44.77
4–HCOO [−]	2.63 (r), 2.32 (C1)	0.14	45.36	47.23	48.02
5–F [−]	1.52 (C2)	0.52	65.37	69.68	71.49
5–Cl [−]	2.51 (C2)	0.34	39.98	42.32	43.30
5–HCOO [−]	2.54 (r)	0.05	44.30	45.85	46.50
6–F [−]	1.45 (C1)	0.53	79.31	84.09	86.11
6–Cl [−]	2.00 (C1)	0.75	44.81	48.57	50.15
6–NO ₃ [−]	(r)	0.06	39.90	41.37	41.99
6–ClO ₄ [−]	2.71 (r)	0.04	37.66	39.26	39.93
7–F [−]	1.50 (C1)	0.50	69.29	73.14	74.76
7–Cl [−]	2.17 (C1)	0.59	41.87	44.41	45.49
7–HCOO [−]	(r)	0.06	46.72	48.45	49.18
7–N ₃ [−]	2.37 (C1)	0.30	49.73	51.85	52.74

^a For other isomers, see Table S2 in the Supporting Information.

^b Distance between the aromatic carbon (Cx) or ring center (r) and the interacting atom in the anion. ^c Charge derived from Natural Population Analysis (NPA) and obtained by subtracting the calculated halide charge from the unit charge of the free halide.

^d Values in bold are the complexes with the highest binding energies for each anion.

although deformation is still observed in the aromatic ring. For comparison, F[−] and Cl[−] σ complexes of tetracyanobenzene (interaction with C–H instead of C–CN) have lower binding energies of 53.1 and 29.8 kcal/mol, respectively, while those of tricyanobenzene have binding energies of 44.1 and 22.7 kcal/mol, respectively, at the MP2/aVDZ level.^{4a}

The Y-shaped HCOO[−] also forms a σ complex with **1** (representative molecular orbital (MO) shown in Figure 4), with a slightly higher binding energy than **1**–Cl[−] and an aromatic C–O bond length of 2.31 Å. On the other hand, **2** complexes with NO₃[−] and ClO₄[−] have much lower q_{CT} as compared to the corresponding halides. However, mixing of orbitals is observed in **2**–NO₃[−] as in weak σ complexes. Because the distinction between anion–π and weak σ interactions is not well-defined for nonspherical anions, the type of interaction in **2**–NO₃[−] and **2**–ClO₄[−] cannot be identified with certainty. Binding energies for **2**–NO₃[−] and **2**–ClO₄[−] are 30.2 and 27.6 kcal/mol, respectively, lower than **2**–Cl[−]. Anion–π complexes of Cl[−] and NO₃[−] with triazine, on the other hand, have much lower binding energies of ~7 kcal/mol, respectively, at the MP2/aVDZ level.^{3a} The H-bond complex of Cl[−]–triazine also has a lower binding energy of ~10 kcal/mol.^{4a}

Halides preferentially attack the C1 carbon of **4**, which has a more positive charge. F[−] forms a strong covalent σ interaction with one of the C1 carbons (1.47 Å) with a binding energy of 73.0 kcal/mol. Cl[−], on the other hand, interacts with both C1 carbons (2.60 Å) with a binding energy of 44.8 kcal/mol. A potential energy scan along the C1–C1 axis in Figure 5 shows that the complex is most stable and charge transfer is most effective when Cl[−] is above the midpoint of the C1–C1 bond. **4**–HCOO[−] has one of its O atoms above the center of the ring (2.63 Å) and the other interacting with one of the C1's (2.32 Å) and has a higher binding energy than the Cl[−] complex of 48.0 kcal/mol. The corresponding complex with N₃[−] is not a minimum structure (Table S2). In the fused, two-ring system **5**, a C2 attack by

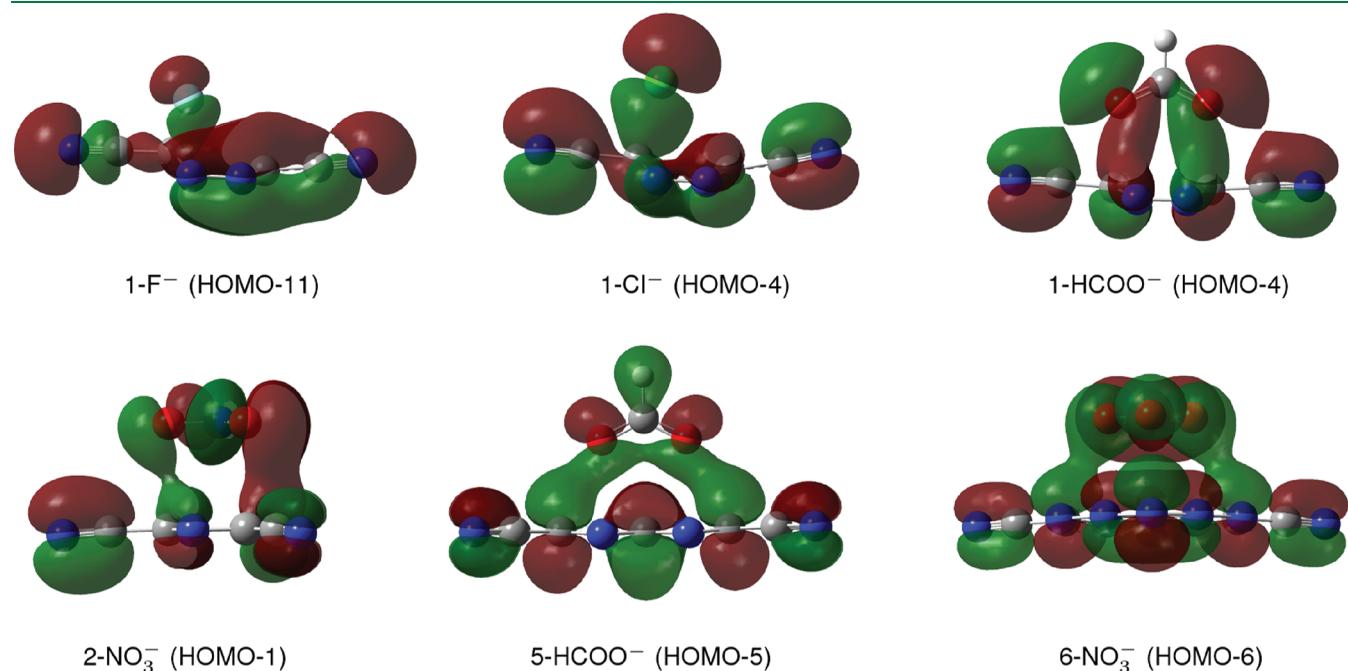


Figure 4. Representative molecular orbitals (MOs) of various anion complexes showing mixing of anion and arene orbitals. MOs rendered at 0.020 ($\text{e} \text{\AA}^{-3}$)^{1/2} isovales.

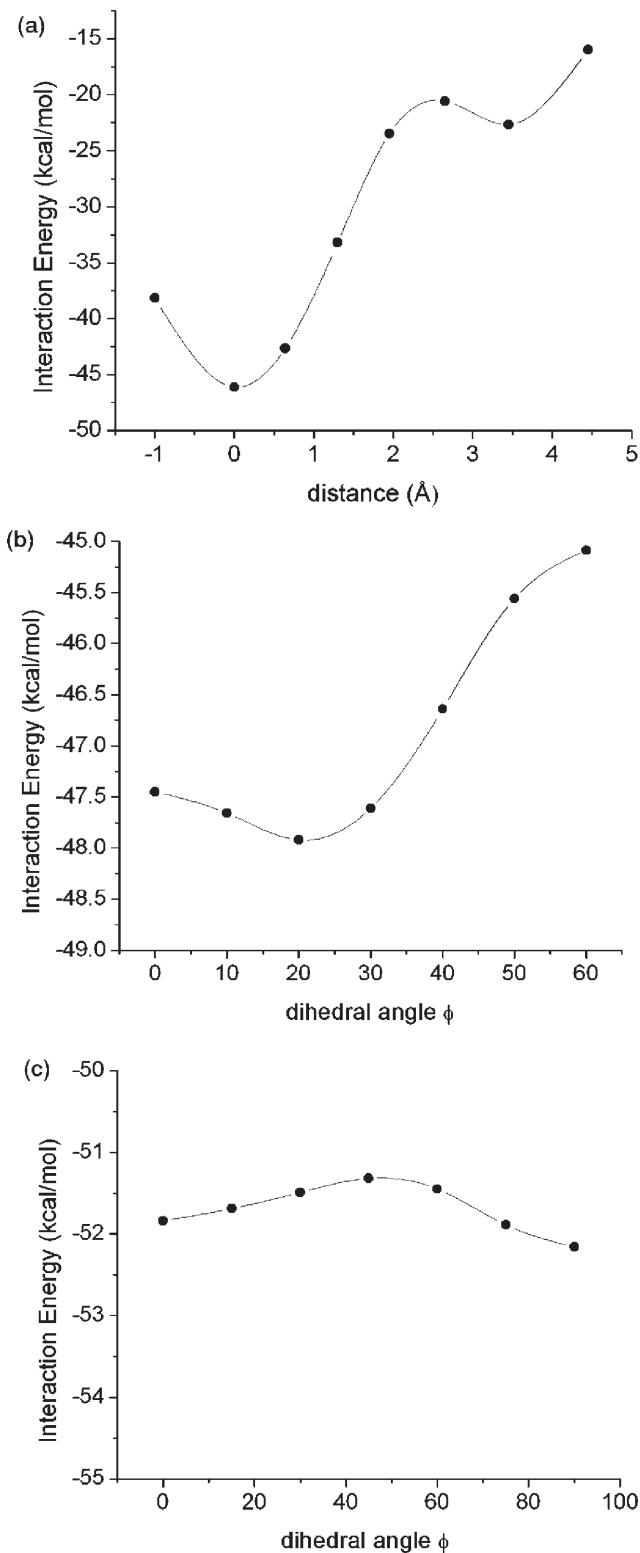


Figure 5. Potential energy scans for (a) $4-\text{Cl}^-$ along the C_1-C_1 axis (distance relative to the midpoint of the C_1-C_1 bond), (b) $6-\text{NO}_3^-$ along the $\text{O}-\text{N}-\text{N}-\text{C}_2$ dihedral angle, and (c) $7-\text{HCOO}^-$ along the $\text{O}-\text{O}-\text{C}_1-\text{C}_1$ dihedral angle. Energies were calculated at the MP2/aug-cc-pVDZ level.

F^- and Cl^- is more favorable despite less positive charge because C_1 is flanked by two negatively charged N atoms. The O atoms of

HCOO^- point toward the center of the ring at a distance of 2.54 Å. As with the complex **4**, $5-\text{HCOO}^-$ has a larger binding energy of 46.5 kcal/mol than the Cl^- complexes. The representative MO of $5-\text{HCOO}^-$ shows mixing of orbitals despite the relatively low q_{CT} value. Complexes of **5** with NO_3^- and ClO_4^- have imaginary frequencies (Table S2).

NO_3^- and ClO_4^- form complexes with the three-ring system **6**, with the O atoms interacting with the ring centers instead of the 3 C_{1s} along the 3-fold rotational axis of **6**. A potential energy scan along the $\text{O}-\text{N}-\text{N}-\text{C}_2$ dihedral angle ϕ in the $6-\text{NO}_3^-$ complex (Figure 5) shows that an eclipsed conformation ($\phi = 60^\circ$) results in a less stable complex. This is consistent with the molecular electrostatic potential (MEP) of **6** indicating that the electrostatic potential is most positive at the ring centers, despite the negative charge of the central nitrogen (-0.43 au). It has been demonstrated that the influence of substituents on the MEP is transmitted through-space, and hence does not necessarily imply local changes in the electron density.²⁰ Both F^- and Cl^- form strong σ interactions with C_1 . Binding energies with **6** are the highest among all of the F^- (86.1 kcal/mol), Cl^- (50.2 kcal/mol), NO_3^- (42.0 kcal/mol), and ClO_4^- (39.9 kcal/mol) complexes considered in the study. Corresponding complexes of Cl^- , NO_3^- , and ClO_4^- with cyameluric acid (=O substituent instead of CN) have been previously reported, but these have much lower binding energies.^{3b}

$7-\text{F}^-$ and $7-\text{Cl}^-$ involve interaction with C_1 with binding energies of 74.8 and 45.5 kcal/mol, respectively. The linear anion N_3^- has a strong σ interaction with the C_1 atoms with the binding energy of 52.7 kcal/mol. In contrast, the O atoms of HCOO^- interact with the ring centers, as in $5-\text{HCOO}^-$, with a binding energy of 49.2 kcal/mol. However, a potential energy scan along the $\text{O}-\text{O}-\text{C}_1-\text{C}_1$ dihedral angle of the $7-\text{HCOO}^-$ complex shows that the energy difference between different orientations, including one for which the O atoms point toward the C_1 atoms ($\phi = 0^\circ$), is not significant (less than 1 kcal/mol). As shown in the MEPs of **5** and **7**, the region above the ring centers also has the most positive electrostatic potential. A $7-\text{NO}_3^-$ complex with the same geometry as $7-\text{HCOO}^-$ is also a minimum albeit with a lower binding energy. On the other hand, the isomers of $7-\text{HCOO}^-$ and $7-\text{NO}_3^-$ wherein the O atoms interact with C_1 have imaginary frequencies. The corresponding anion complex of **7** with the tetrahedral ClO_4^- is not a minimum structure as well (Table S2).

CONCLUSIONS

In summary, strong binding of anions is exhibited by extended Lewis acidic aromatic rings, and selective recognition is accomplished by matching the geometry and charge distribution between anion and arene. The halides F^- and Cl^- form the most stable complex with **6**, while the linear N_3^- only forms a minimum structure with **7**. These complexes are characterized by σ interaction with the most positive aromatic C . The Y-shaped HCOO^- forms the most stable complex with **7**, where the O atoms interact with the ring centers. The trigonal NO_3^- and tetrahedral ClO_4^- fit the 3-fold rotational axis of **6**. However, complexes of these anions with **5** and **7** are not minimum structures. The type of interaction for HCOO^- , NO_3^- , and ClO_4^- cannot be identified conclusively because characteristics of anion- π and weak σ interaction are not well-defined for nonspherical anions. However, they are characterized by weak charge transfer (<0.1 au), so they are less susceptible to solvent

influences.^{5c} The effect of solvation on the stability of σ complexes is beyond the scope of the present study; however, the role of explicit solvation on anion complexation has been reported in a previous study.^{5c} It can be seen that the most stable complexes show the best geometrical fit between guest and host, reminiscent of Lego blocks. Thus, tailoring extended electron-deficient arenes to bind polyanions of a specific geometry and charge distribution provides a strategic method in the design of selective neutral anion receptors and anion-based self-assembly architectures.

■ ASSOCIATED CONTENT

Supporting Information. Structures and interaction energies of low-lying energy complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENT

This work was supported by KRF (National Honor Scientist Program, 2010-0020414, WCU: R32-2008-000-10180-0) and KISTI (KSC-2011-G3-02).

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