

Structural Criteria for the Design of Anion Receptors: The Interaction of Halides with Electron-Deficient Arenes

Orion B. Berryman,[§] Vyacheslav S. Bryantsev,[†] David P. Stay,[§]
Darren W. Johnson,^{*,§} and Benjamin P. Hay^{*,†}

Contribution from the Department of Chemistry, 1253 University of Oregon, Eugene, Oregon 97403, and the Oregon Nanoscience and Microtechnologies Institute (ONAMI), Chemical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352

Received May 17, 2006; E-mail: dwj@uoregon.edu; ben.hay@pnl.gov

Abstract: This paper refines the nature of the interactions between electron-deficient arenes and halide anions. Conclusions are based on (i) new crystal structures containing alkali halide salts with 1,2,4,5-tetracyanobenzene (TCB) and 18-crown-6, (ii) evaluation of crystal structures found in the Cambridge Structural Database, and (iii) MP2/aug-cc-pVDZ calculations of F⁻, Cl⁻, and Br⁻ complexes with TCB, 1,3,5-tricyanobenzene, triazine, and hexafluorobenzene. When the halide lies above the plane of the π system, the results establish that three distinctly different types of complexes are possible: strongly covalent σ complexes, weakly covalent donor- π -acceptor complexes, and noncovalent anion- π complexes. When aryl C-H groups are present, a fourth type of interaction leads to C-H...X⁻ hydrogen bonding. Characterization of the different geometries encountered with the four possible binding motifs provides criteria needed to design host architectures containing electron-deficient arenes.

Introduction

Anion complexation by synthetic host molecules is an important theme in supramolecular chemistry.¹ One of the key challenges is the design of hosts that recognize specific anions. A variety of reversible and/or noncovalent interactions have been used to overcome these challenges, including hydrogen bonding, electrostatic interactions, hydrophobic effects, and coordination to metal ions. A relatively new anion binding motif, the anion- π interaction, has attracted substantial attention in the recent literature. In this interaction, a negatively charged species is attracted to the center of a *charge neutral* electron-deficient aromatic ring as shown in Figure 1.²⁻⁵ Although much of the evidence for the anion- π interaction has come from theoretical

studies,²⁻¹³ there is mounting experimental support for an attractive interaction between anions and electron-deficient arenes from both X-ray structures¹⁴⁻¹⁶ and solution data.^{14,17-19} Recently we,¹⁸ along with others,^{11,12,19} have begun to investigate the utility of the anion- π interaction by deliberately incorporating electron-deficient arenes as binding sites within receptors designed to target anions.

[§] University of Oregon.

[†] Pacific Northwest National Laboratory.

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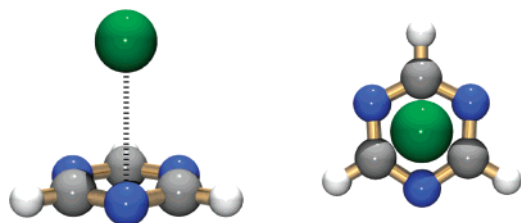


Figure 1. Initial theoretical observation of anion- π complexes occurred in a study of the interaction between Cl^- and triazine.²

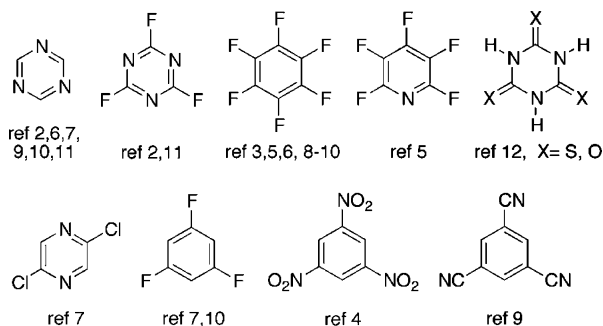


Figure 2. Electronic structure calculations have established that noncovalent anion- π complexes form between halide anions and these electron-deficient arenes.

Anion- π complexes involving halides have been the most widely modeled, and calculated structures have been reported for a variety of arenes (Figure 2).^{2–12} In these structures, the halide is located directly over the center of the arene ring. It has been established that this interaction is predominantly a noncovalent one, dominated by two components: (i) attraction between the negative charge of the anion and the electric field of the arene and (ii) anion-induced polarization. Despite the fact that calculations have found the strength of the anion- π interaction to be significant, typically ranging from 10 to 20 kcal mol⁻¹, there are surprisingly few reports of crystal structures that illustrate this interaction for free halides,^{12,14,15} and there are no examples of halide complexes with any of the unsubstituted arenes that have been studied *in silico* (Figure 2).

Although theoretical studies have focused primarily on the noncovalent anion- π interaction, an experimental study on the solution behavior of halide complexes with highly electron-deficient arenes (Figure 3) suggests that a different binding motif may be operating in these systems.¹⁴ Intense color changes were observed upon addition of halide salts to acetonitrile/dichloromethane solutions containing these arenes. Analysis of the visible spectral data revealed that the halide salts form classic electron donor-acceptor charge-transfer (CT) complexes with the organic π acceptors. This behavior is not consistent with a noncovalent anion- π interaction in which, by definition, there would be negligible CT. Moreover, crystal structures of alkylammonium halide salts with TCP and o-CA revealed the anions to be positioned over the periphery of the arene rings rather

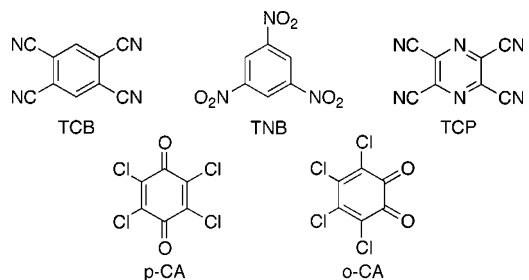


Figure 3. Solution and solid-state studies of these highly electron-deficient arenes yield data inconsistent with a noncovalent anion- π interaction.¹⁴

than over the center of the rings as anticipated for bonding arising primarily from electrostatic and polarization interactions.

This discrepancy between theory and experiment, coupled with the general paucity of structural data for anion- π interactions with arenes such as those depicted in Figures 2 and 3, prompted us to undertake further investigations. To obtain additional structural information, alkali halide salts have been crystallized from solutions containing 1,2,4,5-tetracyanobenzene (TCB) and 18-crown-6. As described herein, the off-center geometries of the halide-arene complexes observed in these structures suggest an alternate interaction motif to the centered noncovalent anion- π interaction widely promulgated in the literature. Electronic structure calculations on halide complexes with TCB and other electron-deficient arenes confirm the presence of alternate binding geometries in which the halide is positioned over the periphery of the ring and there is substantial CT from the halide donor to the π acceptor. Analysis of the Cambridge Structural Database reveals that when halides interact with electron-deficient π systems, they are more likely to reside over the periphery of the ring than over the center, suggesting that the CT binding motif is more common than the noncovalent one. The results indicate that molecular design strategies for incorporating electron-deficient π systems within host architectures should consider the differing geometries attendant with CT versus noncovalent binding motifs.

Methods

General. 1,2,4,5-Tetracyanobenzene was obtained from TCI. Acetonitrile and dichloromethane were obtained from Aldrich and stored over 3 Å molecular sieves. 18-Crown-6 as well as the potassium and sodium salts were obtained from commercial suppliers without the need for further purification.

Single-Crystal Growth. Single crystals suitable for X-ray diffraction were grown by slow evaporation of acetonitrile/dichloromethane solutions at room temperature. TCB (0.030 g, 0.168 mmol), 18-crown-6 (0.100 g, 0.378 mmol), and KI or NaI (0.972 mmol) were added to acetonitrile (1 mL). The resulting suspension was sonicated and heated to reflux. The remaining dark red solution was evaporated at room temperature to yield dark purple crystals of the form $[\text{K}(18\text{-crown-6})(\text{TCB})_2]^+\text{I}^-$ or $[\text{Na}(18\text{-crown-6})(\text{TCB})_2]^+\text{I}^-$. The corresponding KBr structure, $[\text{K}(18\text{-crown-6})(\text{TCB})_2]^+\text{Br}^-$, was obtained in an analogous manner substituting KBr (0.116 g, 0.972 mmol) and a 9:1 dichloromethane/acetonitrile solution as the solvent. Evaporation at room temperature resulted in orange single crystals of the KBr complex.

X-ray Diffraction. Single-crystal X-ray diffraction data for the $[\text{K}(18\text{-crown-6})(\text{TCB})_2]^+\text{Br}^-$, $[\text{K}(18\text{-crown-6})(\text{TCB})_2]^+\text{I}^-$, and $[\text{Na}(18\text{-crown-6})(\text{TCB})_2]^+\text{I}^-$ compounds were collected on a Bruker-AXS SMART APEX/CCD diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.7107$ Å) at 152 K. Diffracted data have been corrected for Lorentz and

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polarization effects and for absorption using SADABS.²⁰ The structures were solved by direct methods, and the structure solution and refinement were based on $|F|$.² All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas all hydrogen atoms were located and given isotropic U values 1.2 times that of the atom to which they are bonded. All crystallographic calculations were conducted with SHELXTL.²¹ Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers 606748, 606749, and 606750. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: international code + (1223)336-033; email: deposit@chemcrs.cam.ac.uk).

Electronic Structure Calculations. Electronic structure calculations were carried out with the NWChem program²² using second-order Möller–Plesset perturbation theory (MP2).²³ Geometries were optimized using the augmented correlation consistent double- ζ basis set (aug-cc-pVDZ)²⁴ and frozen core approximation in the correlation treatment. Tight geometry optimization cutoffs were employed since standard optimization criteria may result in spurious negative frequencies. Frequency calculations were performed at the same level of theory to characterize each stationary point as a minimum or a transition state. The electrostatic potential fit charges²² and NPA natural charges²⁵ were calculated using HF/aug-cc-pVDZ electron densities.

Cambridge Structural Database Searches. The Cambridge Structural Database²⁶ was searched for examples in which a halide anion was located within 4.0 Å of the centroid of any six-membered ring in which all ring atoms were connected to exactly three other atoms. A total of 591 hits were obtained when the search was subject to the following general constraints: (i) R -factor less than 0.10, (ii) no disorder, and (iii) error free. Visual inspection revealed that the majority of the π systems were either positively charged or bound to a positively charged atom. A much smaller subset of this data was retained after applying the additional constraints that either the molecule containing the π system is charge-neutral or when the π system occurred in a positively charged molecule, the positive charge is at least two bonds removed from the π system. This yielded 30 examples most representative of the neutral electron-deficient arenes that have been studied theoretically.^{2–12} To examine the behavior when the π system is in contact with a positive charge, we extracted a larger subset of the data, 138 fragments, in which the halide interacts with an arene ring containing a single nitrogen atom bound to a metal cation (Figures 13 and 14 in Results and Discussion).

A second search was performed to investigate the assertion that there is a preference for neutral electronegative atoms to be located over the center of perfluoroarenes.³ A hit was counted if (i) an electronegative atom F, Cl, Br, I, O, S, or N was within 4.0 Å of the centroid of any pentafluoroarene; (ii) the contact was intramolecular or intermolecular;

(iii) the R -factor was less than 0.05; (iv) there was no disorder; and (v) there was no error. This search yielded a total of 8077 fragments. A subset of this data, 1578 fragments, was obtained after applying the additional constraint that the electronegative atom must simultaneously contact all six carbon atoms of the arene, where each contact distance was less than the sum of van der Waals radii + 1.0 Å (Figure 15, Results and Discussion).²⁷

Results and Discussion

TCB Crystal Structures. Further structural information for the anion– π interaction was obtained by growing single crystals in which TCB interacts with halide anions. TCB, 18-crown-6, and alkali halide salts were dissolved in acetonitrile (KBr) or 9:1 dichloromethane/acetonitrile (KI, NaI) solvent and thoroughly mixed. The purpose of the 18-crown-6 was to enhance the solubility of the salts in organic solvent. Slow evaporation at room temperature yielded single crystals suitable for X-ray diffraction.

Solutions of 18-crown-6 and TCB are colorless. As anticipated,¹⁴ addition of the alkali halide salts produced color changes consistent with the formation of CT complexes. When KBr was added, the solution became bright yellow yielding orange single crystals of $[\text{K}(18\text{-crown-6})(\text{TCB})_2]^+\text{Br}^-$. When KI or NaI were added, the solution became red yielding dark purple single crystals of $[\text{K}(18\text{-crown-6})(\text{TCB})_2]^+\text{I}^-$ and $[\text{Na}(18\text{-crown-6})(\text{TCB})_2]^+\text{I}^-$.

The KBr salt crystallizes in the space group $P2_1/c$, whereas the KI and NaI salts crystallize in the space group $P1$. All three structures exhibit some common features. The alkali cations are encircled by the 18-crown-6 macrocycle. Two TCB ligands are coordinated to each cation via CN nitrogen atoms, with one above and one below the plane of the macrocycle yielding a total coordination number of 8. As illustrated in Figure 4, the crystals pack with alternating cation-bearing layers of 18-crown-6 and anion-bearing layers formed by interlaced axial TCB ligands. The structures differ in the orientation of the TCB groups. In the KBr salt, the planes of the two TCB ligands attached to each cation are roughly perpendicular to one another, whereas, in the KI and NaI salts, they are roughly parallel to one another.

Despite the packing differences, the local environment about each halide anion is remarkably similar in all three crystals. As illustrated in Figure 5, four TCB molecules contact each anion. Distances for these contacts are given in Table 1. There are three distinct orientations: above the arene plane nearest to a carbon bearing a CN group (a and b), above the arene plane nearest to a carbon bearing a hydrogen atom (c), and nearly within the plane of the arene, contacting a C–H hydrogen atom (d).

Orientation d provides a clear example of an aryl C–H \cdots anion hydrogen bond,^{2,28,29} whereas the nature of the interactions represented by the other orientations is not as obvious. In orientations a–c, the anions are located 2.7 to 3.4 Å above the plane of the arene. The anions are not, however, located over

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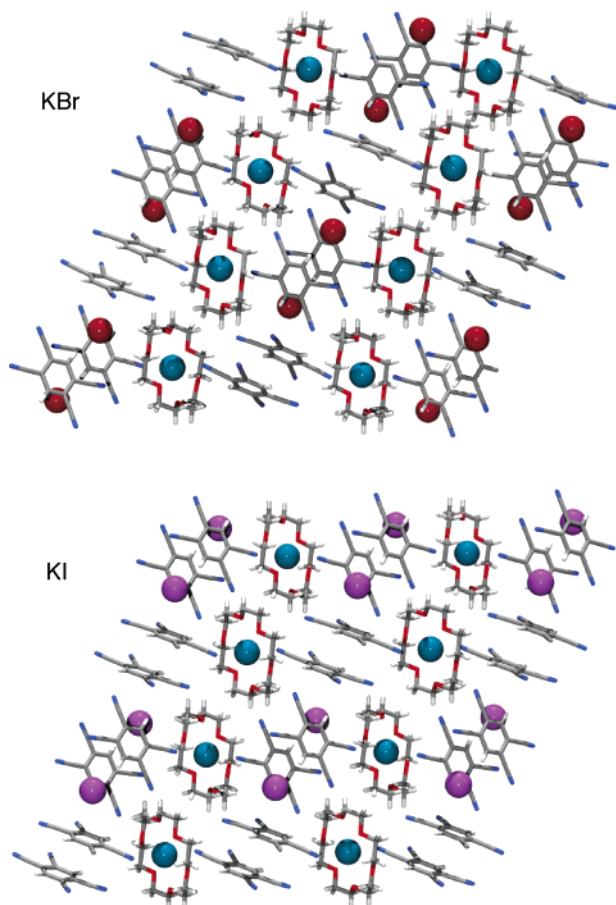


Figure 4. View down the *b*-axis of the KBr structure (top) and the *a*-axis of the KI structure (bottom). The NaI structure (not shown) exhibits the same packing as that of the KI structure. Atom color scheme: C, gray; H, white; N, blue; O, red; K, turquoise; Br, magenta; I, purple.

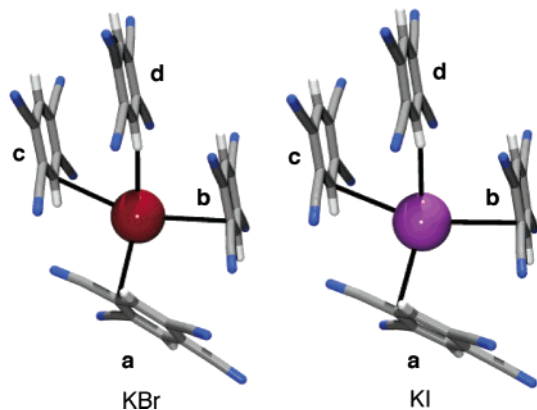


Figure 5. Arrangement of four TCB molecules around the anion is remarkably similar in all structures. The closest contact to each arene is indicated by a black bond.

the center of the arene as anticipated for the noncovalent anion- π interaction. This is clearly illustrated in Figure 6 which shows the halide positions above the TCB plane as well as those previously observed for halide complexes with the similar TCP arene.¹⁴ In every case, the halide anion is positioned either over the periphery of the arene ring or outside the arene ring altogether.

Electronic Structure Calculations. Electronic structure calculations at the MP2/aug-cc-pVDZ level of theory were

Table 1. Observed Halide to Arene Distances (\AA)^a

structure	TCB ^b	d_{carbon}	d_{centroid}	d_{plane}
KBr	a	3.34	3.88	3.26
	b	3.42	4.00	3.16
	c	3.48	4.46	2.72
	d	3.73	5.12	0.60
KI	a	3.45	3.97	3.38
	b	3.60	4.02	3.40
	c	3.56	4.47	3.18
	d	3.90	5.28	0.45
NaI	a	3.46	3.99	3.43
	b	3.57	4.03	3.35
	c	3.53	4.39	3.05
	d	3.90	5.29	0.33

^a Distance between halide and nearest arene carbon atom (d_{carbon}), distance between halide and arene centroid (d_{centroid}), and distance between halide and mean plane of arene (d_{plane}). ^b See Figure 5 for structures.

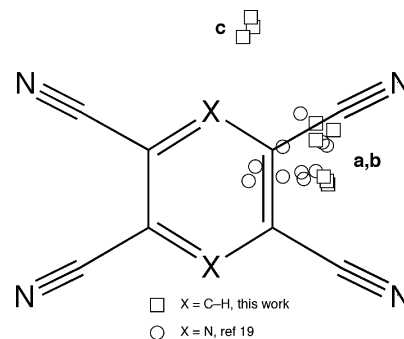


Figure 6. Squares (TCB) and circles (TCP) show the locations of halide anions above tetracyanoarene π systems that have been observed in crystal structures.

performed to evaluate the structure and interaction energies of 1:1 complexes formed between TCB and F^- , Cl^- , and Br^- anions. Four geometries were evaluated for each halide. These include the noncovalent anion- π complex (**1**), a CT complex in which the halide is positioned above a C-H bond (**2**), a CT complex in which the halide is positioned above a C-CN bond (**3**), and a C-H hydrogen bond complex (**4**). Figure 7 illustrates these geometries for Cl^- , and Table 2 summarizes the results obtained for all halides.

Initial calculations focused on the noncovalent anion- π complex, **1**. Somewhat to our surprise, **1** was not a minimum on this potential surface for any of the halides and could only be located by imposing C_{2v} symmetry during the optimization. Prior theoretical studies have established that strongly nucleophilic anions, such as F^- , always interact with electron-deficient arenes by engaging in nucleophilic attack on an arene carbon.^{2-8,10} Thus, the required imposition of symmetry constraints to compute anion- π complexes involving F^- is well-established. However, this is the first instance where it has been necessary to impose symmetry constraints to obtain anion- π complexes for Cl^- and Br^- .

Structure **1** is not a stable geometry for halide-TCB complexes, whereas two alternate geometries have been located for complexes in which the halide lies above the arene plane. In the global C_s symmetry minimum (**2**), the halide lies outside the perimeter of the aromatic ring above a C-H bond. This form is observed for F^- , Cl^- , and Br^- . In the less stable C_1 symmetry minimum (**3**) the halide lies outside the perimeter of

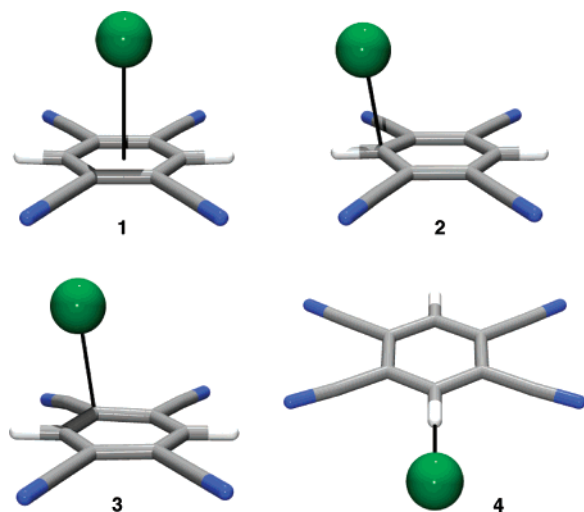


Figure 7. MP2/aug-cc-pVDZ optimized geometries for Cl^- complexes with TCB.

the aromatic ring above a C–CN bond. This form is observed for F^- and Cl^- but is not a stationary point for Br^- .

In the case of F^- , **2** and **3** are much more stable than **1**, by 19 and 13 kcal mol⁻¹, respectively. The F–C distances of 1.50 and 1.58 Å are only slightly longer than the average F–C_{arene} bond length of 1.35 ± 0.02 Å observed in the CSD. The carbon atom bonded to F^- adopts an sp³ geometry. Such geometries, which indicate a strongly covalent interaction, have been described previously in studies of nucleophilic substitution on aromatic rings and are denoted as Meisenheimer or σ complexes.^{30,31}

In the case of Cl^- and Br^- , structures **2** and **3** are close in energy to transition state **1**, but more stable by 0.8 to 1.5 kcal mol⁻¹. The X–C distances are much longer than the average X–C_{arene} distances observed in the CSD: 2.60 and 2.67 Å versus 1.73 ± 0.2 Å for Cl; 2.79 Å versus 1.90 Å for Br. Although there is some distortion to the arene ring, the carbon atom nearest to the halide exhibits a geometry that is closer to that expected for sp² hybridization. As will be discussed below, these structures represent weakly covalent donor to π -acceptor complexes with smaller amounts of CT than observed for F^- .

Finally, geometry **4** confirms that halides also form stable complexes with TCB by hydrogen bonding to one of the C–H groups. Recent theoretical studies have established that arene C–H donor groups form moderate to strong hydrogen bonds with anions.²⁸ The presence of electron-withdrawing substituents increases the acidity of arene C–H donors and, thus, strengthens the interaction.²⁹ The presence of four CN substituents in TCB yields quite acidic C–H groups, so much so that during the optimization of the F^- complex the TCB is actually deprotonated yielding a complex between HF and the TCB anion. Structure **4** contains the strongest arene C–H...Cl⁻ bond yet calculated, with an electronic bonding energy of -27.0 kcal mol⁻¹ compared to values of -16.0 kcal mol⁻¹ for nitrobenzene and -8.6 kcal mol⁻¹ for benzene.²⁹

Insight into the nature of the bonding interactions in **1–4** was obtained by evaluating the extent of CT from the halide donor to the TCB acceptor. Natural Bond Order (NBO) methods²⁵ can be used to estimate the extent of CT by removing the full set of off-diagonal matrix elements between two fragments of the NBO Fock matrix and recalculating the total energy to determine the associated variational energy change. The leading CT interaction between the filled halide lone pair (n) and unfilled antibonding acceptor orbital (φ^*) of electron deficient aromatics is characterized by the second-order stabilization energy $\Delta E^{(2)}$, which represents the strength of the $n \rightarrow \varphi^*$ CT delocalization.

Leading interactions and $\Delta E^{(2)}$ values for complexes **1–4** with F^- , Cl^- , and Br^- are given in Table 2. The $\Delta E^{(2)}$ values are less than 1 kcal mol⁻¹ for all halides with **1**, consistent with the view that the interaction is predominantly noncovalent in nature. Significant amounts of CT are observed in all other cases. The $\Delta E^{(2)}$ values for F^- complexes with **2–4** exceed 200 kcal mol⁻¹, indicative of strongly covalent bonding. In contrast, $\Delta E^{(2)}$ values for Cl^- and Br^- complexes with **2–4** are moderate in value indicating a smaller, but definite, CT interaction.

Covalent bonds can be visualized as regions of electron density between atoms. The lack of CT in **1** and the presence of CT in **2–4** can be observed by rendering the electron density surfaces for these complexes. Figure 8 shows the electron density surfaces for the Cl^- complexes computed at an isovalue of 0.02 eÅ⁻³. There is a gap between the halide and TCB surfaces in **1**, but the surface between the halide and TCB is continuous in **2–4**. This result clearly illustrates that the degree of covalent bonding between the halide and TCB is significantly greater in **2–4** than it is in **1**.

Atomic charges provide another gauge of the extent of CT. Two different approaches, Natural Population Analysis (NPA) and Electrostatic Potential Fit (ESP), were used to obtain the charge distributions in **1–4**. The NPA method derives the charge distribution from the basis functions that are used to represent the wave function.²⁵ The ESP method, which has been used in prior studies of anion- π interactions,^{7–9} derives the charge distribution by fitting the electrostatic potential of the complex. In either case, the extent of CT from the halide to the arene, q_{CT} , is obtained by subtracting the computed halide charge from the unit charge of the free halide.

Values for q_{CT} , given in Table 2, reveal that the NPA values differ substantially from the ESP values. The q_{CT} values obtained with the NPA method are fully consistent with both the results of the NBO analysis ($\Delta E^{(2)}$ values in Table 2) and the evaluation of electron density surfaces (Figure 8). In other words, NPA charges indicate very little CT for **1** and significant CT for **2–4**. In contrast, the ESP charges erroneously indicate a significant CT from the halide to TCB in all cases. The greatest discrepancy occurs with **1**, where the ESP method overestimates q_{CT} by more than an order of magnitude. Thus, although ESP charges do an excellent job of reproducing the mid to far range electrostatic potential of a molecule,³² they fail to adequately describe the extent of CT in the anion- π complex **1**. Failure of the ESP method to represent the charge distribution accurately within other molecules has been noted elsewhere.³³

(30) Such complexes were first reported in: (a) Jackson, C. J.; Gazzolo F. H. *J. Am. Chem. Soc.* **1900**, *23*, 376. A structure was later isolated and characterized in: (b) Meisenheimer, J. *Justus Liebigs Ann. Chem.* **1902**, *323*, 205.

(31) (a) Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667. (b) Strauss, M. J. *Acc. Chem. Res.* **1974**, *7*, 181. (c) Bernasconi, C. F. *Acc. Chem. Res.* **1978**, *11*, 147.

(32) Besler, B. H.; Merz, K. M.; Kollman, P. A. *J. Comput. Chem.* **1990**, *11*, 431.

(33) Wiberg, K. B.; Rablen, P. R. *J. Comp. Chem.* **1993**, *14*, 1504.

Table 2. Calculated Halide to Arene Distances (\AA),^a Electronic Binding Energies (ΔE , kcal mol⁻¹),^b Natural Bond Order Analysis of Charge Transfer Interactions,^c and Charge Transfer from the Anion to the Arene (q_{CT} , e) Derived from Natural Population Analysis (NPA) or Electrostatic Potential Fitting (ESP) for Complexes of F⁻, Cl⁻, and Br⁻ with TCB (1–4), Tricyanobenzene (5–8), Triazine (9–11), and Hexafluorobenzene (12–13)

complex	d_{carbon}	d_{centroid}	d_{plane}	ΔE (binding energy)	leading CT interaction	$\Delta E^{(2)}$	q_{CT} (NPA)	q_{CT} (ESP)
1(F ⁻) [‡]	2.777	2.400	2.400	-33.93(2) ^d		< 1	0.008	0.221
2(F ⁻)	1.500	2.427	1.676	-53.06	$n_4(\text{F}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	> 200	0.477	0.464
3(F ⁻)	1.575	2.537	1.642	-47.24	$n_4(\text{F}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	> 200	0.461	0.426
4(F ⁻)	2.590	4.073	0.000	-45.09	$n_4(\text{F}^-) \rightarrow \sigma^*_{\text{C}-\text{H}}$	> 200	0.274	0.354
1(Cl ⁻) [‡]	3.272	2.962	2.962	-28.34(1) ^d		< 1	0.009	0.180
2(Cl ⁻)	2.603	3.212	2.622	-29.80	$n_4(\text{Cl}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	21.16	0.120	0.237
3(Cl ⁻)	2.673	3.206	2.677	-29.13	$n_4(\text{Cl}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	14.20	0.116	0.244
4(Cl ⁻)	3.151	4.582	0.000	-27.00	$n_4(\text{Cl}^-) \rightarrow \sigma^*_{\text{C}-\text{H}}$	44.92	0.116	0.103
1(Br ⁻) [‡]	3.416	3.122	3.122	-27.70(1) ^d		< 1	0.009	0.178
2(Br ⁻)	2.788	3.349	2.812	-28.68	$n_4(\text{Br}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	15.76	0.107	0.224
4(Br ⁻)	3.325	4.753	0.000	-25.33	$n_4(\text{Br}^-) \rightarrow \sigma^*_{\text{C}-\text{H}}$	37.68	0.086	0.097
5(F ⁻) [‡]	2.841	2.475	2.475	-25.49(2) ^d		< 1	0.007	0.212
6(F ⁻)	1.500	2.474	1.607	-44.10	$n_4(\text{F}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	> 200	0.477	0.484
7(F ⁻)	1.791	2.672	1.811	-34.55	$n_4(\text{F}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	120.0	0.281	0.343
8(F ⁻)	2.527	3.992	0.000	-35.87	$n_4(\text{F}^-) \rightarrow \sigma^*_{\text{C}-\text{H}}$	153.6	0.175	0.197
5(Cl ⁻) [‡]	3.343	3.038	3.038	-21.52(2) ^d		< 1	0.007	0.168
6(Cl ⁻)	2.728	3.370	2.691	-22.72	$n_4(\text{Cl}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	14.35	0.086	0.205
7(Cl ⁻) [‡]	2.837	3.289	2.846	-21.85(1) ^d	$n_4(\text{Cl}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	3.67	0.049	0.182
8(Cl ⁻)	3.204	4.638	0.000	-21.63	$n_4(\text{Cl}^-) \rightarrow \sigma^*_{\text{C}-\text{H}}$	36.72	0.078	0.093
5(Br ⁻)	3.490	3.198	3.198	-21.18		< 1	0.007	0.159
6(Br ⁻)	2.904	3.500	2.876	-21.91	$n_4(\text{Br}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	11.44	0.078	0.194
8(Br ⁻)	3.377	4.808	0.000	-20.29	$n_4(\text{Br}^-) \rightarrow \sigma^*_{\text{C}-\text{H}}$	31.07	0.072	0.092
9(F ⁻) [‡]	2.845	2.179	2.179	-10.92(2) ^d		< 1	0.010	0.155
10(F ⁻)	1.513	2.321	1.673	-26.34	$n_4(\text{F}^-) \rightarrow \pi^*_{\text{N}=\text{C}}$	> 200	0.444	0.382
11(F ⁻)	2.686	4.034	0.000	-18.54	$n_4(\text{F}^-) \rightarrow \sigma^*_{\text{C}-\text{H}}$	54.13	0.075	0.080
9(Cl ⁻)	3.397	3.146	3.146	-8.41		< 1	0.007	0.110
10(Cl ⁻)	2.900	3.448	2.896	-8.68	$n_4(\text{Cl}^-) \rightarrow \pi^*_{\text{N}=\text{C}}$	9.60	0.043	0.110
11(Cl ⁻)	3.408	4.736	0.000	-10.50	$n_4(\text{Cl}^-) \rightarrow \sigma^*_{\text{C}-\text{H}}$	17.54	0.036	0.042
9(Br ⁻)	3.553	3.313	3.313	-8.33		< 1	0.006	0.093
10(Br ⁻)	3.093	3.569	3.109	-8.27	$n_4(\text{Br}^-) \rightarrow \pi^*_{\text{N}=\text{C}}$	7.30	0.035	0.097
11(Br ⁻)	3.580	4.906	0.000	-9.83	$n_4(\text{Br}^-) \rightarrow \sigma^*_{\text{C}-\text{H}}$	15.22	0.033	0.041
12(F ⁻) [‡]	2.889	2.530	2.530	-19.18(2) ^d		< 1	0.004	0.201
13(F ⁻)	1.478	2.722	1.096	-26.01	$n_4(\text{F}^-) \rightarrow \pi^*_{\text{C}=\text{C}}$	> 200	0.501	0.593
12(Cl ⁻)	3.367	3.064	3.064	-16.03		< 1	0.004	0.161
12(Br ⁻)	3.511	3.223	3.223	-15.55		< 1	0.004	0.148

^a Distance between halide and nearest arene carbon atom (d_{carbon}), distance between halide and arene centroid (d_{centroid}), and distance between halide and mean plane of arene (d_{plane}). ^b $E(\text{complex}) - E(\text{halide}) - E(\text{arene})$ using absolute energies obtained at the MP2/aug-cc-pVDZ level of theory. ^c The leading charge-transfer interaction between the filled halide donor lone pair and unfilled acceptor orbital with associated second-order perturbation energies ($\Delta E^{(2)}$, kcal mol⁻¹). ^d Complex is not a minimum on this potential surface. The number of negative frequencies is given in parentheses.

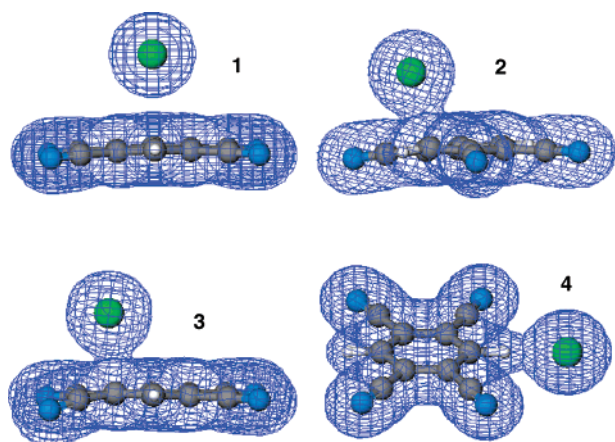


Figure 8. Electron density surfaces for Cl⁻ complexes 1–4, rendered at the same isovalue (0.02 e \AA^{-3}) for comparison, clearly illustrate that the interactions in 2–4 possess a higher degree of CT than that in 1.

This theoretical analysis of TCB halide complexes provides the first example in which noncovalent anion- π complexes are not stable for Cl⁻ and Br⁻. These halides do interact with the arene π system, but the interaction involves CT and in the resulting geometries the anion is located over the periphery of

the ring rather than over the center of the ring. Since prior studies on Cl⁻ and Br⁻ have focused almost exclusively on noncovalent anion- π complexes, there has been virtually no investigation to determine whether such donor- π -acceptor complexes exist for other arenes.³⁴ To address this question, further calculations were performed on halide complexes with 1,3,5-tricyanobenzene, triazine, and hexafluorobenzene. Geometries investigated are illustrated in Figure 9, and results are summarized in Table 2.

Results obtained for 1,3,5-tricyanobenzene are similar to those obtained for TCB. The anion- π structure, **5**, is not a minimum for F⁻ and Cl⁻ but is a stable form for Br⁻. The alternate CT form (**6**) is the global minimum for all three halides. In **6**, the halide is positioned over a C–H bond. The less stable CT complex (**7**) in which the halide is positioned over a C–CN bond, is a stable structure for F⁻, a transition state for Cl⁻, and was not located as a stable point for Br⁻. A C–H hydrogen bond form (**8**) is also a stable structure for all three halides. A previous study of the 1,3,5-tricyanobenzene complex with Br⁻ reported only structure **5**.⁹

(34) Table 1 of ref 2 refers to a stable “attack” complex formed by Cl⁻ and trifluorotriazine. This is the only reported instance where a donor- π -acceptor complex was calculated for Cl⁻, Br⁻, or I⁻.

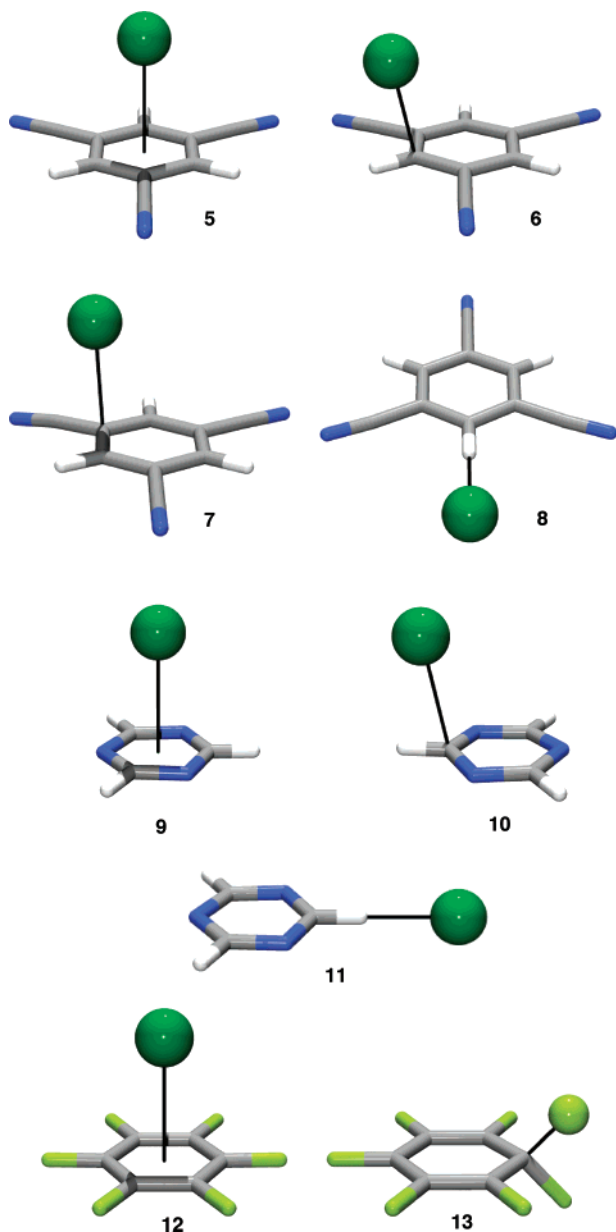


Figure 9. MP2/aug-cc-pVDZ optimized geometries for Cl^- complexes with 1,3,5-tricyanobenzene, **5–8**, triazine, **9–11**, and F^- complex with hexafluorobenzene, **13**.

Three geometries were located for triazine halide complexes. The anion- π structure (**9**) is not a stable point for F^- but is a stable form for Cl^- and Br^- . The alternate CT form (**10**) and a C-H hydrogen bond form (**11**) are minima for all three halides. The CT form is the global minimum for F^- , but the C-H hydrogen bond forms yield the most stable geometries for Cl^- and Br^- . The latter two halides, **9** and **10**, are close in energy, with **10** being the more stable form for Cl^- and **9** being the more stable form for Br^- . The results for F^- are fully consistent with an earlier theoretical study of triazine.² Although **9** and **11** have previously been identified as minima for Cl^- and Br^- ,² none of the prior theoretical studies report the existence of structure **10** for either Cl^- or Br^- .^{2,6,7,9,11}

Two geometries were located for hexafluorobenzene complexes. The anion- π structure (**12**) is not a stable point for F^- but is a stable geometry for Cl^- and Br^- . The alternate CT form (**13**) is the global minimum for F^- but was not located as a

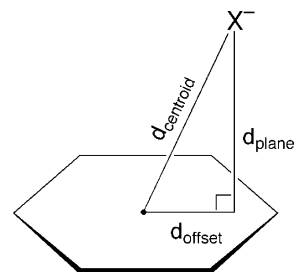


Figure 10. Degree of displacement of a halide, X^- , from the center of an arene is given by d_{offset} . This parameter is calculated from distances (d_{centroid} and d_{plane}) that can be queried in a CSD search to provide $d_{\text{offset}} = (d_{\text{centroid}}^2 - d_{\text{plane}}^2)^{1/2}$.

stable point for either Cl^- or Br^- . These results are completely consistent with prior theoretical studies of this system.^{3,5,6,8–10}

As with **1–4**, the extent of the CT in **5–13** was evaluated via NBO methods and charge distributions. Inspection of Table 2 reveals that all anion- π complexes, **1**, **5**, **9**, and **12**, are characterized by low $\Delta E^{(2)}$ values and q_{CT} (NPA) values of less than $0.01 e$. Values of q_{CT} obtained by the ESP method are greatly overestimated for all these structures. Alternate forms have been identified that involve CT from the halide to the π system, **2**, **3**, **6**, **7**, **10**, and **13**. In these cases, F^- yields high $\Delta E^{(2)}$ values and q_{CT} (NPA) values approaching $0.5 e$ indicative of the formation of strong σ bonds. The other halides are characterized by intermediate $\Delta E^{(2)}$ values, ranging from 7.3 to 21.2 kcal mol⁻¹, and smaller q_{CT} (NPA) values, ranging from 0.03 to 0.12 e .

In three out of the four arenes studied, Cl^- and Br^- are found to form stable, off-center CT complexes with the electron-deficient π system. With one exception, the Br^- complex **10**, these CT complexes are more stable than the noncovalent anion- π complexes. However, the differences in energy are small, ranging from 0.3 to 1.5 kcal mol⁻¹, suggesting a relatively flat potential surface for positioning the halide above the arene plane.

Further Analysis of Single-Crystal Structure Data. The preceding theoretical evaluation of halide complexes with electron-deficient arenes has established that (i) the centered noncovalent anion- π complex is not the most stable structure for the majority of systems reported herein and (ii) CT complexes exist in which the halide is positioned over the periphery of the π system. In both types of complexes, Cl^- , Br^- , and I^- lie 2.5 to 3.5 Å above the arene plane as determined from crystal structures and computations. The type of interaction is structurally distinguished by the location of the halide with respect to the arene center. In the anion- π complex, the halide is located directly over the center. In the CT complex, the halide is located over the periphery of the ring.

As shown in Figure 10, the distance d_{offset} provides a geometric parameter for describing the location of the halide anion. d_{offset} is readily obtained from two other distances, the distance to the centroid, d_{centroid} , and the distance to the average plane of the arene, d_{arene} . The d_{offset} parameter has a value of 0 Å for an idealized, centered anion- π complex. If a halide were positioned directly above a carbon atom in benzene, d_{offset} would be 1.4 Å. Thus, d_{offset} values <0.7 Å are closer to the arene center and would indicate an anion- π interaction, and d_{offset} values >0.7 Å are closer to the arene periphery and would indicate a CT complex. In structures calculated for Cl^- CT

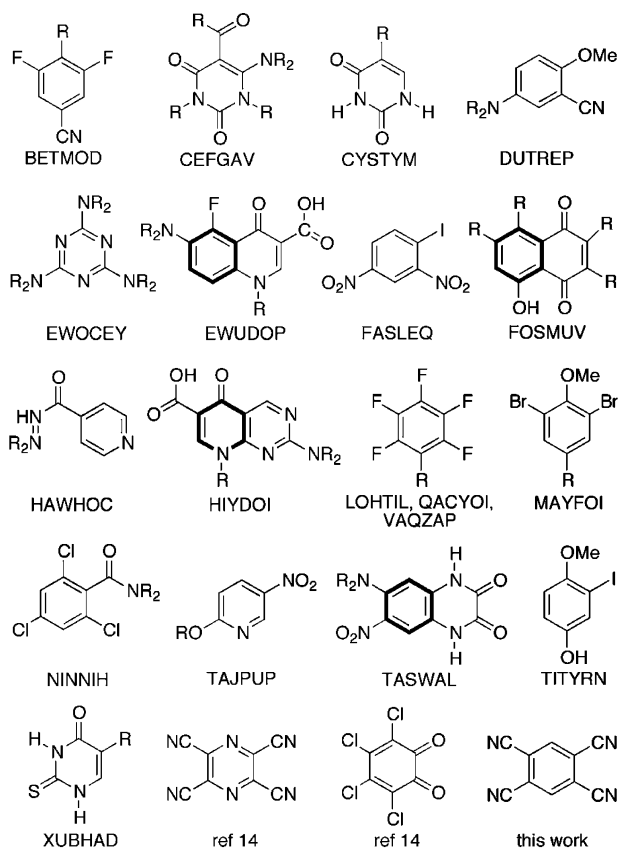


Figure 11. Electron-deficient arenes and CSD recodes for structures in which a halide is located ≤ 4.0 Å from the arene centroid. When more than one ring is present, the ring interacting with the halide is shown in bold.

complexes **2**, **3**, **6**, **7**, and **10**, d_{offset} ranges from 1.7 to 2.0 Å; in crystal structures determined for 1,2,4,5-tetracyanoarenes (see Figure 6, interactions **a** and **b**), d_{offset} ranges from 0.7 to 2.4 Å.

Further evidence for CT interactions between halides and electron-deficient arenes is provided from a survey of the Cambridge Structural Database (CSD). A search for halide anions located within 4.0 Å of the centroid of six-membered ring π systems yielded nearly 600 examples. In most of these cases, however, the π system was either positively charged or bonded directly to a positively charged atom. Retaining only charge-neutral π systems yielded the much smaller set of 19 structures shown in Figure 11. Within these structures there are 30 halide–arene complexes. Distances for these complexes were evaluated yielding the following ranges: d_{centroid} , 3.2 to 4.0 Å; d_{plane} , 3.0 to 3.9 Å; d_{offset} , 0.2 to 2.5 Å. The frequency of d_{offset} values is presented as a histogram in Figure 12. Few structures show the halide positioned near the center of the ring; rather, the distribution exhibits a maximum centered at $d_{\text{offset}} = 1.5$ Å, just outside the ring perimeter. In fact, 84% of the anions in the data set are closer to the ring carbons ($d_{\text{offset}} > 0.7$ Å) than to the centroid. Thus, available structural data indicate the CT motif to be more prevalent than the anion– π motif.

To examine the behavior when the π system is in contact with a positive charge, a larger subset of the data was evaluated. There are 138 examples in which a halide interacts with an arene ring containing a single nitrogen atom bonded to a metal cation. These examples include ligands such as pyridine, bipyridine, 1,10-phenanthroline, etc. Distances for these complexes were evaluated yielding the following ranges: d_{centroid} , 3.3 to 4.0 Å;

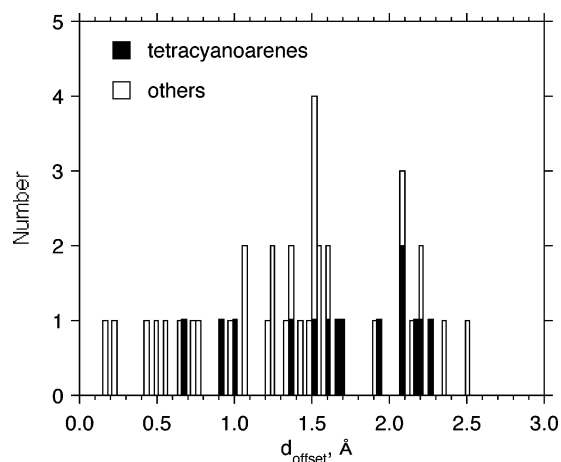


Figure 12. Histogram of d_{offset} values (see Figure 10) for halide complexes with structures shown in Figure 11.

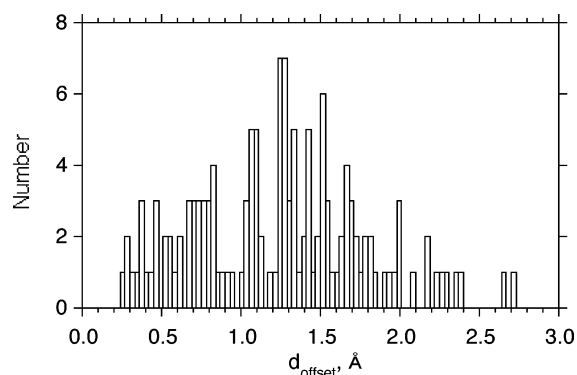
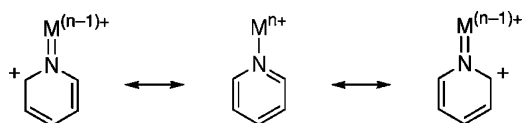


Figure 13. Histogram of d_{offset} values (see Figure 10) for halide complexes with pyridine fragments that are bound to a metal cation.

d_{plane} , 2.6 to 3.9 Å; d_{offset} , 0.3 to 2.7 Å. A histogram of the d_{offset} values for these complexes is shown in Figure 13. As with charge-neutral arenes (Figure 12), the distribution shows a maximum above the ring perimeter and 84% of the anions observed are closer to a ring carbon than to the centroid. These data again suggest the CT motif to be the predominant mode of interaction.

Further insight into the nature of these interactions is obtained by locating the positions of the halides above the pyridine π systems. A plot of these positions, shown in Figure 14, reveals that there is a preference for the halide to locate over the 2 or 6 carbon atom. This positional predilection is in accord with a previous CSD study³⁵ of nitrogen heterocycles interacting with NO_3^- , ClO_4^- , BF_4^- , and PF_6^- as well as being consistent with a CT bonding motif that is stabilized by the following resonance forms:³⁶



The histograms presented in Figures 12 and 13 lead to the conclusion that halide anions are more likely to interact with an electron-deficient π system through a CT motif rather than

(35) Ahuja, R.; Samuelson, A. G. *CrystEngComm* **2003**, *5*, 395.

(36) We do not observe a preference for the anion to be located over the para-position. Possible explanations include (i) electrostatic attraction between the anion and metal cation and (ii) the electropositive metal center inductively stabilizing anion binding at the ortho-positions more than at the para-position.

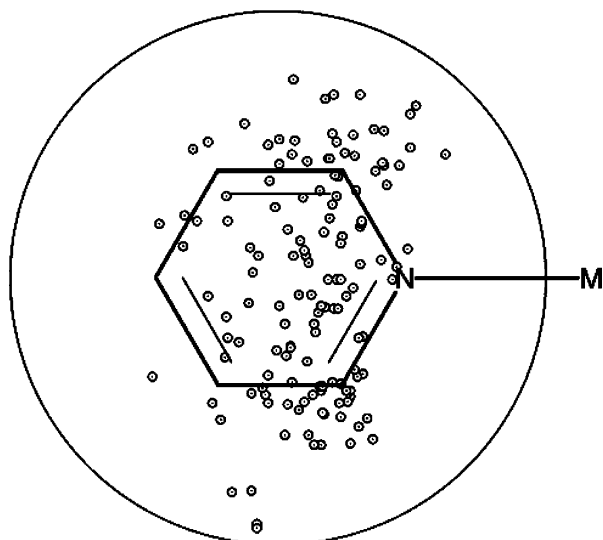


Figure 14. Locations of halide anions above the plane of pyridine fragments that are bound to a metal cation. The pyridine metal complex is drawn to scale, and the circle represents a d_{offset} value of 3.0 Å.

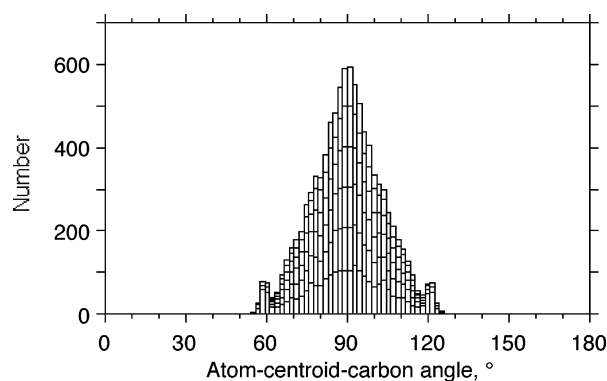


Figure 15. Histogram of the distribution of atom-centroid-carbon angles for electronegative atoms in contact with all six carbon atoms of pentafluoroarenes. All six angles for each hit are plotted.

the anion- π motif. This is contrary to two prior analyses of the CSD, which report evidence of a marked preference for charge-neutral atoms bearing lone pairs to position themselves over the center of pentafluoroarenes³ and trinitrobenzene derivatives.⁴ In these analyses, the database was searched for instances in which any electronegative atom F, Cl, Br, I, O, S, or N was in contact with all six carbon atoms of the arene, where each contact distance was defined as the sum of van der Waals radii + 1.0 Å.²⁷ Evidence in support of the anion- π interaction was provided by histograms of atom-centroid-carbon angles showing that data were concentrated at angles close to perpendicular to the ring, consistent with a preference for an electronegative atom to reside above the arene centroid.

In an effort to resolve the inconsistency, this analysis was repeated for pentafluoroarenes. Figure 15 shows that it is possible to reproduce the previously reported histogram very closely.³ However, such data are misleading and give rise to false conclusions regarding the location of electron-rich atoms positioned above electron-deficient arenes. First, the atom-centroid-carbon angle is a poor indicator for the location of an atom above the arene plane. When the atom is off-center, the angle obtained depends on the choice of carbon atom. It is possible for two of the six angles to be near 90°, even when the atom lies well outside the ring perimeter. In addition, these

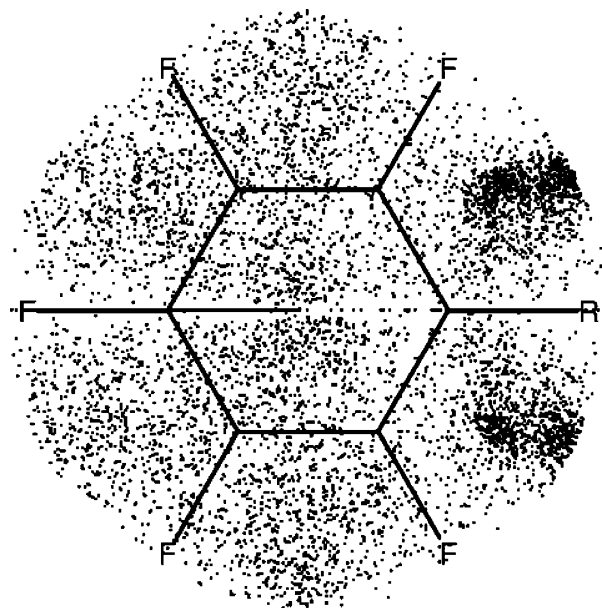


Figure 16. Locations of electronegative atoms above the pentafluoroarene plane. The arene is drawn to scale, and the outer perimeter represents a d_{offset} value of 3.0 Å.

angles are not a very sensitive measure of the degree of displacement. For example, if the atom is constrained to be 3.5 Å above the arene plane and to lie within a perpendicular plane containing a pair of para carbon atoms, the atom-centroid-carbon angle involving one of these para carbon atoms varies with d_{offset} as follows (angle, d_{offset}): 90°, 0 Å; 80°, 0.62 Å; 70°, 1.27 Å; 60°, 2.02 Å. Although the atom-centroid-carbon angles are indeed distributed about 90°, the distribution is wide, ranging from 55° to 126°. Evaluation of d_{offset} values for the data in Figure 15 reveals that, in 65% of the cases, the atom is closer to the ring perimeter than to the centroid (>0.7 Å) and, in 17% of the cases, the atom lies outside the ring perimeter (>1.4 Å).

A second, and perhaps more serious, source of confusion stemming from this search is that constraining the electronegative atom to be in simultaneous contact with all six arene carbon atoms biases the search to select data that tend to lie over the arene. A much larger number of hits are obtained when the search criteria are altered such that the electronegative atom must be within 4 Å of the pentafluoroarene centroid. These hits contain the subset of data used to generate Figure 15. Distances in these structures were evaluated yielding the following ranges: d_{centroid} , 2.4 to 4.0 Å; d_{plane} , 1.8 to 4.0 Å; d_{offset} , 0 to 3.5 Å. The distribution of the electronegative atoms over the pentafluoroarene plane is illustrated in Figure 16. When the atom lies well outside the ring perimeter, a preference to lie in between the ring substituents is apparent. However, for d_{offset} values ranging from 0 to 2 Å, statistical analysis of the data (Supporting Information) shows that charge-neutral electronegative atoms within 4 Å of a pentafluoroarene centroid are distributed randomly over the arene surface; in other words, these data establish the complete absence of any preferred location over this π system.

Summary and Conclusions

In this study, we have used electronic structure calculations and crystal structure data to investigate how halides interact

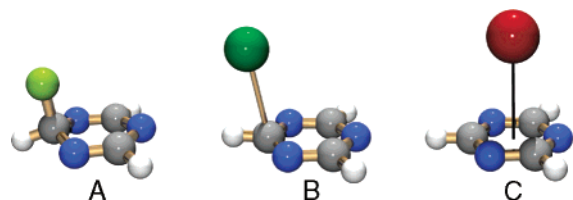


Figure 17. When a halide is located above triazine, the most stable forms are a σ complex with F^- (A), a donor– π -acceptor complex with Cl^- (B), and an anion– π complex with Br^- (C).

with electron-deficient π systems. When the halide lies above the plane of the π system, the results establish that three distinctly different types of complex are possible: strongly covalent σ complexes (A), weakly covalent donor π -acceptor complexes (B), and noncovalent anion– π complexes (C). As shown in Figure 17, examples of all three types occur with triazine. These complexes are distinguished from one another by the extent of CT and the position of the halide above the π system.

Strongly covalent σ complexes result from nucleophilic attack at a ring carbon. These complexes are characterized by a large amount of CT from the anion to the π system. As established in earlier theoretical studies^{2–12} and as confirmed in this study, such complexes represent the only stable geometry that locates F^- above the plane of an aromatic ring. For the complexes investigated here, most F–C bond distances are short, near 1.5 Å. The ring carbon under attack adopts a tetrahedral geometry, and as a result, the F^- anion is located outside the ring perimeter. There is substantial experimental precedent for the formation of stable σ complexes in studies of nucleophilic substitution reactions of electron-deficient aromatic rings.^{30,31} Consistent with these experimental studies, calculations have established that σ complexes also are formed between electron-deficient arenes and other strongly nucleophilic anions. Examples include CN^- and CO_3^{2-} interacting with C_6F_6 ³ and CN^- , NC^- , and CO_3^{2-} interacting with triazine.^{5,6}

Weakly covalent donor– π -acceptor complexes may be formed with less nucleophilic halides. These complexes are characterized by a smaller, but definite, amount of CT from the anion to the π system. Geometries for such complexes are consistent with much less covalent character than in the σ complexes, exhibiting elongated halide–carbon distances and near planar arene carbon atoms. Like σ complexes, the halide is located outside the ring perimeter. Experimental evidence for donor π -acceptor complexes, both in solution and in the solid phase, was provided by a recent study.¹⁴ Further analysis of crystal structure data presented herein confirms that there is a marked preference for halides to lie either over or outside the perimeter of electron-deficient six-membered rings. Results from electronic structure calculations are fully consistent with this result. For example, three out of the four arenes evaluated in this study exhibit calculations that indicate when Cl^- is located above the π system, the donor– π -acceptor motif yields the more stable Cl^- complex.

Noncovalent anion– π complexes may also be formed with less nucleophilic halides. These complexes are characterized by CT values of $\leq 0.01 e$ and a geometry in which the halide is located directly above the arene centroid. Although prior theoretical studies have yielded numerous examples of such complexes in the gas phase,^{2–12} crystal structure analysis reveals that there are relatively few clear examples of anion– π

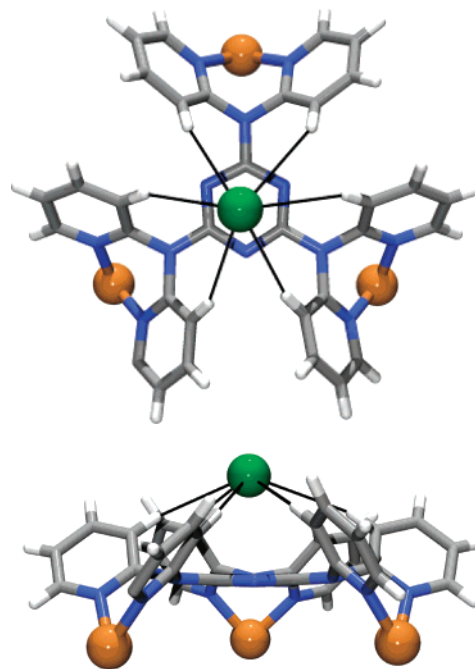


Figure 18. Views of a fragment of a Cl^- receptor¹⁵ crystal structure showing six hydrogen-bonding interactions with aryl C–H groups of Cu(II)-coordinated pyridine rings and one anion– π interaction with a melamine ring. Interaction geometries are near ideal with all C–H $\cdots Cl^-$ angles $\geq 150^\circ$ and Cl^- to C distances ranging from 3.9 to 4.3 Å.

complexes for halides in the solid state. Indeed, the current study has established that when an arene becomes sufficiently electron-deficient, noncovalent anion– π complexes may no longer represent stable geometries for halides larger than F^- . For example, the noncovalent anion– π complexes for Cl^- with TCB and 1,3,5-tricyanobenzene are both found as transition states on the MP2/aug-cc-pVDZ potential surface.

Additionally, one should not overlook the fact that electron-deficient arenes bearing C–H groups are potent hydrogen bond donors. As noted elsewhere, even in the absence of electron-withdrawing substituents, simple arenes form C–H hydrogen bonds with anions that can exceed 50% the strength of those formed by O–H and N–H groups.²⁸ In electron-deficient arenes, aryl C–H groups become much stronger donor groups.²⁹ As shown in Table 2, both tri- and tetracyanobenzene yield hydrogen-bonded complexes with Cl^- and Br^- that are 88 to 95% as strong as corresponding donor– π -acceptor complexes, with interaction energies ranging from -20 to $-27 \text{ kcal mol}^{-1}$. In the case of triazine, C–H hydrogen bonding yields the most stable complexes with Cl^- and Br^- , 18 to 21% more stable than the corresponding anion– π or donor– π -acceptor forms.

The role of aryl C–H binding sites is nicely illustrated in a recent crystal structure.¹⁵ Although attention was drawn to the fact that this structure contains one of the few examples of an anion– π interaction, containing a Cl^- anion positioned above the center of a melamine ring, no mention was made of the interactions with the other electron-deficient arenes lining the binding cavity. As illustrated in Figure 18, C–H groups of Cu(II)-coordinated pyridine rings form six hydrogen bonds with the Cl^- guest. Because each of these aryl C–H groups offers a

more powerful binding site than the melamine π system,³⁷ it is likely that the six C–H hydrogen bonds play the dominant role in determining the position of the anion within this cavity.

This study has refined our understanding of how halides interact with arenes. The existence of four potential binding motifs establishes electron-deficient arenes to be versatile building blocks, augmenting the arsenal of conventional hydrogen bonding and electrostatic components that have been used widely in the construction of anion receptors.¹ The results indicate that molecular design strategies for incorporating electron-deficient arenes within anionophore architectures should consider the quite different geometries encountered for the various interactions. The optimal binding motif for a given arene–anion pair may not be immediately obvious, suggesting that new systems should be evaluated on a case-by-case basis.

Knowledge of preferred binding motifs provides a basis for optimizing host architectures for specific anions. For example, in cases where substantial covalent character is anticipated, such as with strongly nucleophilic anions and/or highly electron-deficient arenes (Figure 3), optimal interaction with the π system will be achieved when the arene building block is oriented so that the anion is able to adopt a position above the ring perimeter. Constraining host architecture so that the guest is only permitted to interact with the edges of the arene could lead to enhanced selectivity for such anions.

The influence of arene orientation is expected to decrease as the extent of CT decreases. Comparison of interaction energies for various binding motifs for Cl^- and Br^- with cyanide-substituted arenes reveals that although the strongest bonding is attained when the halide is positioned outside the ring perimeter, substantial stabilization is retained when the anion

is held over the ring centroid. The insensitivity of interaction energy to anion position is most pronounced in the Br^- complexes with triazine. Although the anion– π and donor– π -acceptor complexes exhibit d_{offset} values of 0 and 1.75 Å, respectively, these two orientations yield essentially the same interaction energy (Table 2).

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Supporting Information Available: Crystallographic data for the complexes $[\text{K}(18\text{-crown-6})(\text{TCB})_2]^+\text{Br}^-$, $[\text{K}(18\text{-crown-6})(\text{TCB})_2]^+\text{I}^-$, and $[\text{Na}(18\text{-crown-6})(\text{TCB})_2]^+\text{I}^-$ (CIF files). The full citation for ref 22, Cartesian coordinates and energies (Hartrees) for the MP2/aug-cc-pVDZ optimized geometries for **1–13**, and a statistical analysis showing that the data in Figure 16 are randomly distributed over the arene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(37) The C–H groups in Cu(II)-coordinated pyridine are more acidic than those in benzene. Thus, the strength for one of these interactions should exceed $-8.6 \text{ kcal mol}^{-1}$.^{28,29} With three electron-donating amine substituents, the melamine π system should form weaker complexes than triazine. Thus, the strength of this anion– π interaction should be less than $-8.4 \text{ kcal mol}^{-1}$ (Table 2).