

Can Electron-Rich π Systems Bind Anions?

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ABSTRACT: In general, anion– π interactions exist between anions and aromatics with a positive quadrupole moment. The interaction between anions and aromatics with a negative quadrupole moment is expected to be unstable due to Coulombic repulsion. However, here we investigated the cases of aromatics with a negative quadrupole moment such as electron-rich alkyl/alkenyl/alkynyl-substituted benzenes and triphenylene, which interact with halides. Favorable binding was demonstrated with coupled cluster theory with singles, doubles, and perturbative triples excitations [CCSD(T)] at the complete basis set (CBS) limit. Stability increases with chain length, unsaturation, and halogenation. Energy decomposition analysis based on symmetry adapted perturbation theory (SAPT) shows that electrostatic repulsion is overcome by induction effects arising from the alkyl substituents.

INTRODUCTION

The design of anion receptors is traditionally predicated by interaction of the negatively charged anion with either positively charged or hydrogen bond donor groups or by coordination with metals.¹ Prime examples of this are imidazolium,² the urea complex,³ and quaternary ammonium-salt-based⁴ and calix-[*n*]arene/pyrrole receptors.⁵ Aromatic moieties are a mainstay of anion receptors as a molecular scaffold. For the anion– π interaction,⁶ the π system has generally positive traceless quadrupole moment [$\Theta_{zz} = (3Q_{zz} - \text{Tr}\{Q\})/2$], and thus it is attractive. However, the anion– π interaction when the π system has a negative quadrupole moment is expected to be repulsive because of Coulombic repulsion, so that anion recognition by electron-rich aromatic systems has hardly been explored. Experiments^{7–11} and theoretical calculations^{12–15} on the aromatic systems with a positive quadrupole moment demonstrated attractive interactions for the anion. Recent experimental evidence of anion– π interaction was demonstrated in halide recognition via a copper(II)–azadendtriz complex (containing pyridine units),⁸ tetraoxacalix[2]arene[2]triazine receptors,⁹ pentafluorobenzyl-substituted ammonium and pyridinium salts,¹⁰ and Ag(I)/Cu(I)–tetrazine complexes.¹¹ Desirable properties of π interaction, including directionality and ease of fine-tuning properties through substituents, serve as an impetus in developing anion receptors based on anion– π interaction.

Well-studied model systems include the halide complexes of hexafluorobenzene ($\Theta_{zz} = 9.50 \text{ D}\text{\AA}$), 1,3,5-trinitrobenzene ($\Theta_{zz} = 22 \text{ D}\text{\AA}$), 1,3,5-tricyanobenzene ($\Theta_{zz} = 19.53 \text{ D}\text{\AA}$), and the heteroaromatic *s*-triazine ($\Theta_{zz} = 0.90 \text{ D}\text{\AA}$).^{12–15} In some cases, the total interaction energy of anion– π complexes is comparable to that of cation– π complexes;¹⁶ for instance, the MP2/aug-cc-pVDZ binding energy for $\text{C}_6\text{F}_6\text{--F}^-$ is 18.4 kcal/mol,^{14a} while that of $\text{C}_6\text{H}_6\text{--Na}^+$ is 22.3 kcal/mol.^{16a} Frequency calculations show that only the Cl^- , Br^- , and NO_3^- complexes of triazine and hexafluorobenzene, the Br^- complexes of 1,3,5-tricyanobenzene, and the CN^- complexes of hexafluorobenzene are actual minima in the gas phase.¹⁷ It has been demonstrated that halides preferentially form either a covalent σ or H bond complex as a consequence of electron-withdrawing groups, which increases

the acidity of aryl C–H and activates the ring toward nucleophilic substitution. This is supported by a survey of crystal structures of a neutral six-membered aromatic ring in the Cambridge Structural Database (CSD) wherein 84% of the halides are closer to the ring C than the centroid.¹⁷ A later study¹⁸ defining stringent criteria for the anion– π interaction, specifically the ring atom–anion distance of $\leq \text{vdw} + 0.2 \text{ \AA}$ and the tilt angle of $90 \pm 10^\circ$ (from the ring plane), did not yield a convincing example of anion– π interaction as the aromatic rings are invariably bound to a cationic site. A preliminary study of Cl^- complexes shows that the majority of samples have Cl^- at θ values $< 20^\circ$, which is consistent with the H bonding motif.

While most models of anion– π complexes are not actual minima, theoretical calculations are nevertheless important in shedding light on the nature of anion– π interactions. A symmetry-adapted perturbational theory (SAPT) analysis of complexes of tetrafluoroethene, hexafluorobenzene, and triazine with halides (F^- , Cl^- , Br^-) and linear (CN^-) and trigonal planar (NO_3^- , CO_3^{2-}) anions shows that the most significant contributions to the interaction energy come from electrostatic and induction effects.^{14a} As in cation– π complexes, dispersion effects are relatively low in comparison to the other energy components. Electrostatic effects dominate at large distances, but induction effects become more significant as the distance decreases. The induction contribution is attributed to the interaction of the occupied p orbital of halides or the π orbital of organic anions with the lowest unoccupied molecular orbital (LUMO) of the aromatic ring.

As stated above, anion binding with aromatics of negative Θ_{zz} is expected to be unstable due to Coulombic repulsion. However, it has already been demonstrated^{15,19} that there is no correlation between Θ_{zz} and the anion binding enthalpy, unlike the case of cation complexes, which implies that anion– π interaction is, in fact, possible for aromatics with negative Θ_{zz} if the induction overcompensates for the electrostatic repulsion. Recently, experimental evidence of anion– π interaction between electron-rich

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alkylbenzene rings and F^- , in combination with $(C-H)^+ \cdots F^-$ type ionic bonds, was reported for an imidazolium cage receptor.²⁰ It was particularly noted that the nonalkylated analogue cannot host F^- in the cavity between the two benzene rings that form a sandwich complex. The CCSD(T)/CBS calculations on the triethylbenzene moiety yielded an interaction energy of -0.9 kcal/mol.²⁰ A theoretical study by Wheeler and Houk¹⁵ on model $Cl-C_6H_6-nX_n$ ($n = 0-4, 6$; X is either electron-donating or electron-withdrawing) complexes showed that the interaction energy for trimethylbenzene is slightly attractive (the interaction energy of -0.4 kcal/mol at the M06-2X/6-31+G(d) level). More importantly, it was noted that anion binding can be attributed to direct interaction of the anion with the local dipole induced by the substituents and not with substituent-induced polarization of the π density as previously asserted.¹³ This is consistent with the results of Kim et al.,^{14a} showing a relatively low dispersion contribution in the anion binding of π systems such as hexafluorobenzene. The previous studies suggest that substituents have an important role in overcoming Coulombic repulsion between the negative Θ_{zz} of the aromatic ring and the anion. Moreover, it indicates that the nature of interaction in anion complexes of aromatics with negative Θ_{zz} is different from that with positive Θ_{zz} . Even in π - π interactions, significant differences in geometry and binding energy between electron-deficient and electron-rich aromatics have been observed.²¹

In line with this, the present study investigates the nature of anion- π interaction in aromatic systems with electron-donating alkyl substituents and an electron-withdrawing halogenated-alkyl/alkenyl/alkynyl substituent. Triply substituted benzene was chosen for the study to limit the variable factor to substituent effects. The influence of chain length, unsaturation, and halogenation in the substituent on the electrostatic, induction, dispersion, and exchange-correlation energies will be systematically studied by using high-level ab initio and SAPT calculations. The substituents include methyl (Me), ethyl (Et), $-CH=CH_2$, $-C\equiv CH$, $-CH_2F$, and $-C\equiv CF$, and a fused ring system is considered as well. The results will be discussed in comparison to anion- π complexes of trifluorobenzene, tribromobenzene, and other systems with positive Θ_{zz} . The choice of specific geometry with the anion lying above the ring center was made in order to examine and understand anion interactions with the ring electron density because of its plausible experimental realization in liquid or crystal phases. Despite the fact that the gas phase frequency calculations for such isolated systems of alkylbenzene moieties and F^- yield saddle points, it should be noted that the anion- π type interaction between alkylbenzene moieties and F^- is experimentally realized.²⁰

COMPUTATIONAL METHOD

The resolution of identity approximation of the second-order Møller–Plesset perturbation theory (RIMP2) using the aug-cc-pVDZ (aVDZ) basis set with basis set superposition error (BSSE) correction was used to optimize the geometries of various anion- π complexes. The geometry was constrained to C_{3v} symmetry so that the center of the anion lies along the C_6 axis of the aromatic ring. Vibrational frequency calculations were performed at the same level, while quadrupole moments of the RIMP2/aVDZ geometries were determined at the RHF/6-311G** level. Single point energy calculations were subsequently performed at the RIMP2/aug-cc-pVTZ (aVTZ) and CCSD(T)/

aVDZ levels with BSSE correction to obtain energies at the complete basis set (CBS) limit. The MP2 CBS limit was evaluated by using the extrapolation scheme based on the proportionality of the basis set error in the electron correlation energy to N^{-3} for the aug-cc-pVNZ basis set.²² This was then used to estimate the CCSD(T)/CBS limit by adding the CCSD(T)/aVDZ binding energies and the difference between the MP2/CBS and MP2/aVDZ binding energies.

The total interaction energy was decomposed into electrostatic (E_{es}), induction (E_{ind}), dispersion (E_{disp}), and exchange-repulsion (E_{exch}) components, or effective induction (E_{in}), effective dispersion (E_{dp}), and effective exchange-repulsion (E_x) components based on SAPT,²³ as described previously.²⁴

$$E_{tot} = E_{es} + E_{in} + E_{dp} + E_x$$

where

$$E_{es} = E_{es}^{(10)} + E_{es, resp}^{(12)}$$

$$E_{in} = E_{ind}^{(20)} + E_{exch, ind, resp}^{(20)} + \delta_{ind, resp}^{HF} + {}^tE_{ind}^{(22)} + {}^tE_{exch, in}^{(22)} - 0.4 \\ \times (E_{CCSD(T)/CBS} - E_{SAPT(MP2)/aVDZ'})$$

$$E_{dp} = E_{disp}^{(20)} + E_{exch, disp}^{(20)} + \delta_{ind, resp}^{HF} - 0.6 \\ \times (E_{CCSD(T)/CBS} - E_{SAPT(MP2)/aVDZ'})$$

$$E_x = E_{exch}^{(10)} + E_{exch}^{(11)} + E_{exch}^{(12)}$$

The superscripts refer to orders in the intermolecular interactions and intramolecular correlation potential, “resp” to the inclusion of coupled Hartree–Fock response, and $\delta_{ind, resp}^{HF}$ to higher-order Hartree–Fock induction and exchange-induction contributions. E_{in} is the sum of the exchange-induction term and E_{ind} . E_{dp} is the sum of the exchange-dispersion term and E_{disp} , while E_x excludes the aforementioned terms from E_{exch} . E_{dp} and E_{in} include the difference between the CCSD(T)/CBS and SAPT(MP2)/aVDZ' binding energies to correct for the basis set dependency of the dispersion and induction energy, as discussed in previous studies.²⁴ SAPT calculations were performed with SAPT2008²⁵ at the MP2/aVDZ' level where the p diffuse functions on H and the d diffuse functions on heavy atoms are removed. RIMP2 and CCSD(T) calculations were done using Turbomole 6.0.2²⁶ and Gaussian 09,²⁷ respectively.

RESULTS AND DISCUSSION

Optimized geometries of the F^- complexes of various substituted benzenes, constrained to C_{3v} symmetry, are shown in Figure 1. The complete list of traceless quadrupole moments (Θ_{zz}), perpendicular distance (R_c), and interaction energies are summarized in Table 1, while SAPT components of the interaction energy of selected complexes are listed in Table 2. The focus of the present work is to determine the effect of electron-donating alkyl substituents on the anion- π type interaction; hence these geometries will be used in the discussion despite the fact that these structures are saddle points.

Bz- F^- , with an interaction energy of 0.66 kcal/mol, is unstable with respect to the dissociated F^- and benzene. However, the F^- - π complex becomes stable with methyl (-0.38 kcal/mol)

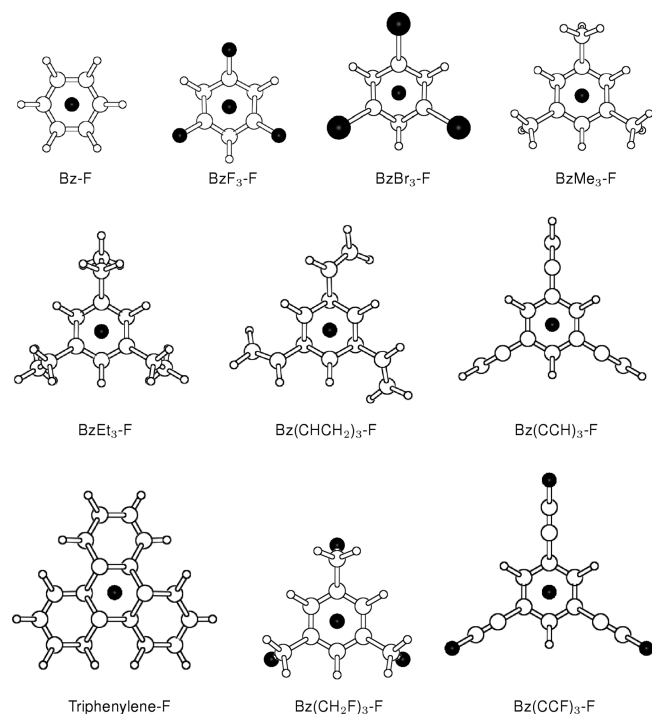


Figure 1. Optimized geometries of various F^- - π complexes obtained at the RIMP2/aVDZ level with BSSE correction.

and ethyl (-0.86 kcal/mol) substitution. The increased stability from $Bz-F$ to $BzEt_3-F$ is accompanied by a decrease in R_v , which caused increased exchange repulsion with chain length. While Θ_{zz} is the least negative in $BzMe_3$, the repulsive electrostatic contribution increases uniformly with chain length, which indicates that the charge-quadrupole interaction is not significant. Wheeler and Houk¹⁵ attributed this to the short distance between the halide and aromatic ring, in which case the expansion of intermolecular electrostatic interactions in terms of electric multipoles cannot be considered valid or accurate. The attractive inductive effects increase from $Bz-F$ to $BzEt_3-F$ due to anion-induced polarization of alkyl substituents, which becomes significant with increasing chain length. Clements and Lewis¹⁹ also showed that favorable anion binding of halo-substituted aromatics arises from the polarizability of the substituents as evidenced by the increase in anion binding with increased number and polarizability of the substituent. The attractive dispersion contribution also increases but is lower than those of other components.

The effect of unsaturation is determined by a comparison of $BzEt_3-F$, $Bz(CHCH_2)_3-F$, and $Bz(CCH)_3-F$. The F^- and Cl^- complexes of $Bz(CCH)_3$ were reported earlier by Wheeler and Houk¹⁵ and Lucas et al.^{13e,f} The increase in stability is dramatic, from -0.86 kcal/mol in $BzEt_3-F$ to -7.11 kcal/mol in $Bz(CCH)_3-F$. The system is further stabilized in fused rings (triphenylene- F), as can be seen from the RIMP2/CBS energies (-7.34 kcal/mol compared to -6.58 kcal/mol in $Bz(CCH)_3-F$). Θ_{zz} becomes more negative with unsaturation, and yet, there is a shift from repulsive to attractive electrostatic energy from $BzEt_3-F$ to $Bz(CCH)_3-F$. The attractive electrostatic term in $Bz(CCH)_3-F$ indicates that the ethynyl group is electron-withdrawing. The increase in attractive induction effects is significant upon unsaturation, while that for dispersion is moderate.

Table 1. BSSE-Corrected RIMP2 and CCSD(T) Interaction Energies (in kcal/mol) on the BSSE-Corrected RIMP2/aVDZ Optimized Geometries^a

complex	Θ_{zz}	R_v	MP2			CCSD(T)	
			aVDZ	aVTZ	CBS	aVDZ	CBS
$Bz-F$	-8.76	3.270	1.72	1.08	0.81	1.57	0.66
$Bz-Cl$	-8.76	3.812	1.01	0.44	0.20	1.37	0.56
$Bz-Br$	-8.76	3.870	0.86	0.20	-0.08	1.38	0.44
$BzMe_3-F$	-8.46	3.157	0.88	0.17	-0.14	0.63	-0.38
$BzEt_3-F$	-9.11	3.080	0.24	-0.28	-0.50	-0.11	-0.86
$BzEt_3-Cl$	-9.11	3.569	-0.54	-1.11	-1.35	-0.05	-0.86
$BzEt_3-Br$	-9.11	3.730	-0.73	-1.34	-1.59	-0.11	-0.97
$Bz(CHCH_2)_3-F$	-15.37	2.829	-1.95	-3.19	-3.71	-2.00	-3.76
$Bz(CCH)_3-F$	-16.99	2.612	-5.47	-6.25	-6.58	-6.00	-7.11
$Bz(CCH)_3-Cl$	-16.99	3.293	-3.71	-4.59	-4.97	-2.95	-4.20
$Bz(CCH)_3-Br$	-16.99	3.486	-3.30	-4.20	-4.58	-2.35	-3.64
triphenylene- F	-25.16	2.439	-6.01	-6.95	-7.34	NA	NA
triphenylene- Cl	-25.16	3.117	-3.26	-4.43	-4.92	NA	NA
BzF_3-F	0.69	2.755	-8.20	-8.68	-8.88	-8.62	-9.31
BzF_3-Cl	0.69	3.330	-6.26	-6.91	-7.19	-5.63	-6.56
BzF_3-Br	0.69	3.517	-5.72	-6.40	-6.69	-4.98	-5.95
$BzBr_3-F$	-3.91	2.658	-10.34	-11.56	-12.07	-10.58	-12.31
$Bz(CH_2F)_3-F$	-6.43	2.736	-13.78	-14.28	-14.48	-13.85	-14.55
$Bz(CH_2F)_3-Cl$	-6.43	3.346	-12.72	-13.35	-13.62	-11.83	-12.74
$Bz(CH_2F)_3-Br$	-6.43	3.516	-12.32	-13.00	-13.28	-11.31	-12.27
$Bz(CCF)_3-F$	-2.65	2.709	-7.56	-8.00	-8.18	-8.67	-9.29
$Bz(CCF)_3-Cl$	-2.65	3.290	-6.00	-6.51	-6.73	-5.45	-6.18
$Bz(CCF)_3-Br$	-2.65	3.479	-5.57	-6.10	-6.33	-4.82	-5.58

^a Θ_{zz} : quadrupole moment of the uncomplexed aromatic system (in DÅ) calculated at the RHF/6-311G** level, R_v : perpendicular distance between the ring centroid and anion in Å. Geometries are constrained to C_{3v} symmetry. Vibrational frequency calculations demonstrate that only BzF_3-Br is a genuine minimum, while $BzMe_3-F$ has 5 imaginary frequencies and the rest have 2 each. Positive interaction energy indicates that the complex is less stable than the dissociated structure.

Table 2. SAPT(MP2)/aVDZ' Energies (in kcal/mol) Calculated Using the BSSE-Corrected RIMP2/aVDZ Geometries

complex	E_{tot}	E_{es}	E_{in}	E_{dp}	E_x
$Bz-F$	0.66	5.69	-7.13	-1.58	3.67
$Bz-Cl$	0.56	3.86	-4.08	-2.29	3.07
$Bz-Br$	0.44	2.99	-3.78	-2.94	4.17
$BzMe_3-F$	-0.38	5.92	-9.41	-1.88	4.99
$BzEt_3-F$	-0.86	6.24	-11.07	-2.11	6.08
$BzEt_3-Cl$	-0.86	3.71	-6.61	-3.72	5.76
$BzEt_3-Br$	-0.97	2.89	-5.65	-4.25	6.04
$Bz(CHCH_2)_3-F$	-3.76	2.07	-14.77	-2.62	11.56
$Bz(CCH)_3-F$	-7.11	-5.66	-17.82	-3.70	20.08
BzF_3-F	-9.31	-10.03	-11.46	-1.95	14.14
BzF_3-Cl	-6.56	-7.53	-5.54	-3.75	10.26
BzF_3-Br	-5.95	-7.19	-4.50	-4.17	9.90
$BzBr_3-F$	-12.31	-10.59	-16.44	-3.34	18.07
$Bz(CH_2F)_3-F$	-14.55	-15.34	-13.10	-1.38	15.28
$Bz(CH_2F)_3-Cl$	-12.74	-13.46	-6.15	-3.53	10.41
$Bz(CCF)_3-F$	-9.29	-5.98	-15.88	-3.12	15.69

Halogenation of substituents increases stability, as demonstrated by $Bz-F/BzF_3-F$ ($0.66/-9.31$ kcal/mol), $BzMe_3-F/Bz(CH_2F)_3-F$ ($-0.38/-14.55$ kcal/mol), and $Bz(CCH)_3-F/Bz(CCF)_3-F$ ($-7.11/-9.29$ kcal/mol). While the Θ_{zz} values of $Bz(CH_2F)_3$ and $Bz(CCF)_3$ are still negative, they are

more positive than their unhalogenated counterparts. There is a shift from repulsive to attractive electrostatic terms and a significant increase in exchange-repulsion due to decreased R_v in the case of $Bz-F/BzF_3-F$ and $BzMe_3-F/Bz(CH_2F)_3-F$. The attractive induction term also increases, similar to the effect of chain length and unsaturation. Attractive dispersion effects increase from $Bz-F$ to BzF_3-F but decrease from $Bz(Me)_3-F$ to $Bz(CH_2F)_3-F$. On the other hand, the attractive electrostatic term from $Bz(CCH)_3-F$ to $Bz(CCF)_3-F$ increases only slightly, while attractive induction and dispersion effects, as well as exchange-repulsion, decrease.

Electrostatic and induction effects are comparable in magnitude in alkyl-substituted benzenes (Bz , $BzMe_3$, $BzEt_3$, and $Bz(CH_2F)_3$) like the case of anion- π complexes of electron-deficient aromatic rings such as hexafluorobenzene, triazine,^{14a} BzF_3 , and $BzBr_3$. However, the electrostatic term is repulsive for Bz , $BzMe_3$, and $BzEt_3$. In the case of unsaturated substituents as in $Bz(CHCH_2)_3$, $Bz(CCH)_3$, and $Bz(CCF)_3$, the attractive induction term is much larger than the electrostatic term. Exchange-repulsion terms have the highest magnitude in the case of hexafluorobenzene and triazine but are comparable to the electrostatic and/or inductive effects in alkyl-substituted benzenes, BzF_3 , and $BzBr_3$. In both electron-deficient and alkyl-substituted benzenes, dispersion effects are relatively low. Unlike the halide complexes of hexafluorobenzene, triazine,^{14a} BzF_3 , $Bz(CCH)_3$, $Bz(CH_2F)_3$, and $Bz(CCF)_3$, the interaction energies for the halide complexes of Bz and $BzEt_3$ become more attractive from F^- to Br^- . The electrostatic energy becomes more attractive in the latter, while the opposite occurs in hexafluorobenzene, triazine,^{14a} BzF_3 , and $Bz(CH_2F)_3$. The induction energy becomes more repulsive in Bz , $BzEt_3$, BzF_3 , and $Bz(CH_2F)_3$ and attractive in hexafluorobenzene.^{14a} This parallels the decrease in electronegativity and the increase in polarizability of the anion from F^- to Br^- . The attractive dispersion energy increases in all cases.

A Cambridge Structural Database (CSD, version 5.31, November 2009) search on possible anion- π interactions between halides, NO_3^- , or ClO_4^- and alkylated arenes with an anion-centroid distance R_v of 5 Å and a tilt angle θ of $90 \pm 15^\circ$ yielded 32, 1, and 4 samples, respectively. All fragments are bonded to positively charged groups. Four samples, all interacting with Br^- , are found to contain trialkylated benzene fragments — $RAJXUW$ ($R=Me$),²⁸ $REQYOC$ ($R=Ph$),²⁹ and $UMICEY/UMICOI$ ($R=Et$).³⁰ Only two samples, $BIHQOZ$,³¹ a macrobicyclic azaphane receptor, and $REQYOC$,³⁵ an N-spiro chiral quaternary ammonium bromide, satisfy the following criteria based on optimized geometries of halide complexes of $BzEt_3$ ($R_v = 3-4$ Å, ring atom-anion distance of $\leq vdw + 0.5$ Å and $\theta = 90^\circ \pm 10^\circ$). In the former, anion recognition is primarily based on CH and NH anion interactions. However, the I^- -centroid distance is 3.692 Å, and all tilt angles are 90° , which is consistent with theoretical calculations on anion- π complexes.

CONCLUSION

The present study demonstrates the presence of anion- π interactions between halides and alkyl/alkenyl/alkynyl-substituted aromatics. An increase in the chain length, unsaturation, and halogenation of the alkyl substituents is paralleled by an increase in stability of the anion- π complex. Despite the repulsive electrostatic term, the F^- complexes of $BzMe_3$, $BzEt_3$, $Bz(CHCH_2)_3$, and $Bz(CCH)_3$ are stable due to attractive

induction effects arising from the substituent. The attractive dispersion contributions are relatively low. The F^- complexes of BzF_3 , $BzBr_3$, $Bz(CH_2F)_3$, and $Bz(CCF)_3$ have an attractive electrostatic term, but these are lower in magnitude than the induction energy, except in the case of $Bz(CH_2F)_3$. Unlike F^- complexes of aromatics with a positive Θ_{zz} like hexafluorobenzene and triazine, the exchange-repulsion is comparable in magnitude to these two terms. The interaction energies become more repulsive from F^- to Br^- in BzF_3 , $Bz(CCH)_3$, $Bz(CH_2F)_3$, and $Bz(CCF)_3$ as in the case of hexafluorobenzene and triazine^{14a} and more attractive in Bz and $BzEt_3$. The attractive anion- π interactions in alkyl-substituted aromatic complexes can be utilized in the design of anion receptors as already demonstrated by imidazolium-based receptors.²⁰

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