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ARTICLE

Predicting the Cation- π Binding of Substituted Benzenes: Energy Decomposition Calculations and the Development of a Cation- π Substituent Constant

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This work proposes a new substituent constant, termed Π^+ , to describe cation- π binding using computational methods at the MP2(full)/6-311++G** level of theory with Symmetry Adapted Perturbation Theory (SAPT) calculations on selected cation- π complexes. The correlations between binding strength (E_{bind} or ΔH_{298}) and common parameters for describing cation- π binding ($\Sigma\sigma_m$, $\Sigma\sigma_p$, $\Sigma(\sigma_m+\sigma_p)$, or Θ_{zz}) are decent (r^2 between 0.79 and 0.90). SAPT calculations show that variations in the electrostatic (E_{ele}), exchange (E_{exch}), induction (E_{ind}), and dispersion (E_{disp}) component energies to the overall binding are almost entirely due to differences in arene-cation distances ($d_{\text{Ar-cat}}$). E_{ele} varies most with $d_{\text{Ar-cat}}$; however, E_{ind} seems to be the primary term responsible for the $\Sigma\sigma_m$, $\Sigma\sigma_p$, $\Sigma(\sigma_m+\sigma_p)$ and Θ_{zz} parameters not accurately predicting the cation- π E_{bind} and ΔH_{298} values. The Π^+ parameter largely reflects electrostatics, but it also includes the impact of exchange, induction, and dispersion on cation- π binding of aromatics, and the resulting correlation between ΔH_{298} or E_{bind} and Π^+ is excellent (r^2 of 0.97 and 0.98, respectively). Importantly, the Π^+ parameter is general to cation- π systems other than those reported here, and to studies where the cation- π binding strength is determined using computational levels different from those employed in this study.

1 Introduction

Cation- π interactions^{1,2} are important in a wide range of chemical and biological fields including enzyme-substrate recognition,^{3,4} catalyst development,^{5,6} and nanomaterial design.⁷ The nature of cation- π interactions was initially described in terms of the aromatic quadrupole moment (Θ_{zz}) and the electrostatic potential (ESP).^{8,9} There is a significant difference in how well they predict cation- π binding energies due to the nature of the two terms. Essentially, the quadrupole moment is part of the multipole expansion series (point charge, dipole, quadrupole, etc.) where the electrostatics of a molecule is described at a single point, while ESPs are defined at each point in space. In most cation- π complexes the interacting species are too close for the multipole expansion series to

converge, thus explaining why ESPs perform better at predicting relative cation- π binding. For instance, the aromatic Θ_{zz} value shows minimal correlation with the cation- π binding enthalpy (ΔH_{298}) values of ten halo- and cyano-substituted aromatics ($r^2 = 0.78$),¹⁰ however, the correlation between the cation- π binding energy (E_{bind}) and the aromatic ESP values for 11 aromatics was quite strong ($r^2 = 0.98$).⁹ Similarly, Suresh and Sayyed very recently reported a study with a large number of substituted benzenes and showed the cation- π binding energies correlate to an excellent degree ($r^2 > 0.97$) with the molecular electrostatic potential (MESP).¹¹ Aromatic Θ_{zz} and ESP values require calculation, and predicting the strength of cation- π interactions via aromatic substituent constants would be more facile. Dougherty and coworkers appear to be the first researchers to suggest a possible relationship between cation- π

binding and Hammett substituent constants,⁹ though most of their work concentrated on the correlation between the binding energies and the aromatic ESPs.⁹ More recently, Hunter and coworkers employed their chemical double-mutant cycles towards the investigation of cation- π binding using the *N*-methyl pyridinium cation, and they found an excellent correlation between the cation- π binding free energy values and the Hammett σ_p value.¹² Additionally, computational work by Jiang and coworkers showed an excellent correlation between the cation- π binding enthalpies of aniline, toluene, phenol, benzene, fluorobenzene, 1,4-difluorobenzene, and 1,3,5-trifluorobenzene and what the authors term the total Hammett parameter, σ_{Total} .¹³ The investigated cations were Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , and Ca^{2+} , and the total Hammett parameter was defined as $\sigma_{\text{Total}} = (\Sigma\sigma_m + \Sigma\sigma_p)$. This is the only example of using σ_{Total} to understand the non-covalent binding of aromatics, and Jiang and coworkers suggest it means both resonance and induction are important in cation- π binding.¹³ Sanderson and coworkers provided an example of using Hammett constants to help elucidate the importance of cation- π binding in biological environments in their studies on the binding of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine to 5-substituted tryptophan analogs.¹⁴

Computational work by Cormier and Lewis on the Li^+ and Na^+ binding of multi-substituted cyclopentadienyl (Cp) anions suggested that cation-substituent interactions were an important factor in Cp-cation binding.¹⁵ Furthermore, an excellent correlation between Cp-cation binding energies and the $\Sigma\sigma_m$ of the Cp anions was demonstrated.¹⁵ Although the binding of cations to Cp anions is not generally viewed as a cation- π interaction, it does involve a cation interacting with the π -face of an aromatic, and it certainly would not be unreasonable to expect the trends found in Cp-cation complexes to extend to more traditional cation- π complexes. In fact, recent work by Wheeler and Houk shows that cation- π E_{bind} values of substituted benzenes can be predicted, to a decent degree ($r^2 = 0.81$), by summing the binding energy due to the cation interacting with the parent benzene and the binding energy due to the cation interacting with the substituent.¹⁶ Based on this result the authors suggest that differences in cation- π binding of substituted aromatics are due to the interaction of the ion and the substituents on the aromatic, rather than to differences in aromatic π -cloud polarization.¹⁶ In a similar vein, Suresh and Sayyed recently discussed the contributions of substituent inductive, resonance, and through-space cation-substituent effects in cation- π interactions of substituted benzenes and, like Houk and Wheeler, they suggest that cation-substituent interactions are an important factor in cation- π interactions of substituted benzenes.¹⁷

The computational work presented here, on a large number of substituted benzenes, shows cation- π ΔH_{298} and E_{bind} values are predicted, to a decent degree, by either the sum of the aromatic Hammett constant σ_p ($\Sigma\sigma_p$), the sum of the aromatic Hammett constant σ_m ($\Sigma\sigma_m$), $\Sigma(\sigma_m + \sigma_p)$, which is the σ_{Total} value proposed

by Jiang and coworkers,¹³ or the aromatic Θ_{zz} value. The sum of the Hammett constants was used since mono- and multi-substituted benzenes were investigated. The correlation with either ΔH_{298} or E_{bind} is best for the $\Sigma(\sigma_m + \sigma_p)$ value; however, it is not substantially better than with the other three parameters. Ultimately, the ΔH_{298} and E_{bind} correlations are almost identical. Symmetry Adapted Perturbation Theory (SAPT) calculations show that variations in substituted benzene cation- π component energies are directly correlated to variations in the cation-arene distance ($d_{\text{Ar-cat}}$). The variations in the dispersion (E_{disp}), induction (E_{ind}), and exchange (E_{exch}) component energies of E_{bind} are only slightly sensitive to $d_{\text{Ar-cat}}$; however, the changes in the electrostatic component (E_{ele}) are very sensitive to $d_{\text{Ar-cat}}$. As a result of the SAPT calculations, the Na^+ -mono-substituted benzene ΔH_{298} values are used to develop a cation-arene binding parameter, which we term Π^+ , that performs much better than any of the Hammett parameters or the aromatic Θ_{zz} values in correlating the cation- π ΔH_{298} or E_{bind} values of mono- and multi-substituted benzenes. The generality of the Π^+ term is demonstrated by exploring its ability to correlate cation- π binding energies determined in other studies.

2 Computational Methods

Sodium cation-substituted benzene complexes, $\text{Na}^+ - \text{C}_6\text{X}_n\text{H}_{(6-n)}$, were investigated where the substituted aromatics have $X = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{NO}_2, \text{CH}_3, \text{OH}, \text{NH}_2, \text{OCH}_3$ and $\text{N}(\text{CH}_3)_2$ substituents with mono-, ortho-di-, meta-di-, para-di-, 1,3,5-tri- and 1,2,4,5,-tetra-substitution patterns. Each Na^+ -substituted benzene complex is referred to using the shorthand **X1**, **X2o**, **X2m**, **X2p**, **X3** and **X4** where **X** is the substituent, the numbers 1 – 4 are the number of substituents, and the letters ‘o’, ‘m’ and ‘p’ indicate whether the di-substituted aromatics are ortho-, meta- or para-substituted. The parent Na^+ -benzene complex is referred to as **C₆H₆**. The **N(CH₃)₂4** complex binding energy was not calculated because of the steric problems associated with having two large groups ortho to each other. The **CN4**, **NO₂3** and **NO₂4** complexes were also not calculated, because the resulting complexes with sodium cation are repulsive. The **NO₂2o** was not included in the study because the ortho nitro groups are significantly out of plane, due to steric repulsion, and this significantly affects the cation- π binding. All substituted benzenes and sodium cation-substituted benzene complexes were optimized, and frequency calculations were performed, at the MP2(full)/6-311++G** level of theory. The resulting structures were characterized as minima by the absence of imaginary frequencies. Some of the optimized structures had imaginary frequencies, as shown in the Supporting Information, and this is not surprising given the tendency for the MP2 method to give anomalous imaginary frequencies for aromatics, which has been explained as arising from a two-electron basis set incompleteness error (BSIE).¹⁸ When these structures were re-optimized at the RHF/6-311++G** level of theory, the resulting frequency calculations did not contain any imaginary frequencies. Two exceptions are the **NO₂1** and **NO₂2p** cation-arene complexes. We have

previously reported that the **NO₂1** complex is not a minimum, and the only cation-arene minimum for Na⁺-C₆H₅NO₂ is the cation-dipole complex.¹⁹ The same explanation applies to the **NO₂2p** complex. For the substituted aromatics containing iodine atoms the MIDI-X basis set was employed for I, while the 6-311++G** basis set was used for all other atoms. The MP2(full)/6-311++G** calculated binding energies were corrected for basis set superposition error (BSSE) using the counter-poise method.²⁰ Cation- π E_{bind} values were determined by subtracting the calculated energies of each substituted benzene and Na⁺ from the BSSE-corrected energy of the respective Na⁺-substituted benzene complex. All reference to MP2(full)/6-311++G** calculated binding energies throughout the remaining text refers to the BSSE corrected values. The ΔH_{298} values were determined via the equation $\Delta H_{298} = E_{\text{bind}} + (E_{\text{Thermal,complex}} - (E_{\text{Thermal,Arene}} + E_{\text{Thermal,Na}^+}))$. Each E_{Thermal} value is obtained via frequency calculation and constitutes the thermal energy correction from vibrational, rotational, and translational energies upon going from 0K to 298K for the Na⁺-C₆X_nH_(6-n) complexes, the arenes, and the Na⁺ cation.

SAPT^{21,22} binding energy decomposition calculations were performed on selected Na⁺-substituted benzene complexes in order to determine the contributions from electrostatics, dispersion, induction and exchange to the overall binding energies. The geometries for the SAPT calculations were the MP2(full)/6-311++G** optimized Na⁺-substituted benzene complex structures. The SAPT monomer wave functions were calculated using the CCSD/6-311++G** theoretical method, using the basis functions for the full dimer. This is the counter-poise approach to determining BSSE-corrected binding energies, and thus the SAPT binding energies reported in this manuscript should be considered BSSE-corrected. All optimization and binding energy calculations were performed using the Gaussian03 suite of programs.²³ The SAPT calculations were done via SAPT2008²⁴ using ATMOL1024,²⁵ or Dalton 2.0,²⁶ as the front end for computing integrals.

The MP2(full)/6-311++G** level of theory was chosen because of the good agreement between the calculated Na⁺-benzene binding energy and the experimental value. There have been three experimentally measured Na⁺-benzene binding enthalpies: $\Delta H_0 = -28.0 \pm 0.1 \text{ kcalmol}^{-1}$,²⁷ $\Delta H_{298} = -22.5 \pm 1.5 \text{ kcalmol}^{-1}$,²⁸ and $\Delta H_{298} = 21.5 \pm 1.0 \text{ kcalmol}^{-1}$.²⁹ Recent high-level computational work supports the accuracy of the latter two values;^{30,31} the calculated Na⁺-benzene binding energy is $\Delta E_0 = -22.95 \text{ kcalmol}^{-1}$ at the CCSD(T) level with complete basis set approximation³⁰ and $\Delta E_0 = -21.5 \text{ kcalmol}^{-1}$ at the MP2 level with the Sadlej basis set.³¹ At the MP2(full)/6-311++G** level of theory the Na⁺ binding energy is $\Delta H_{298} = -18.5 \text{ kcalmol}^{-1}$, just outside the experimental range for the smaller two experimental values.

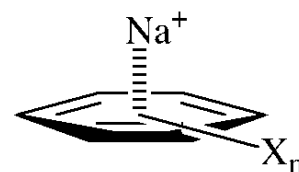
Finally, the aromatic quadrupole moments, Θ_{zz} , were also determined at the MP2(full)/6-311++G** level of theory, using a coordinate system centered at the aromatic ring center. The

aromatic quadrupole moment is a 3 X 3 tensor and for planar, non-polar aromatics the off-diagonal tensor components are zero and $\Theta_{zz} = \Theta_{zz} - 0.5(\Theta_{xx} + \Theta_{yy})$. Of course, not all of the aromatics investigated here are non-polar; the mono-, ortho-di-, and meta-di-substituted aromatics are polar, and the corresponding Θ_{zz} off-diagonal tensor components have non-zero values. However, the magnitudes of these off-diagonal tensor components are less than 10% of the value of the diagonal tensor components, and thus the equation for Θ_{zz} based on the diagonal terms is an excellent approximation of the aromatic Θ_{zz} value for the polar aromatics.

3 Results and Discussion

3.1 Cation- π Binding Energies (E_{bind}) and Enthalpies (ΔH_{298}) of Substituted Benzenes

The cation- π E_{bind} and ΔH_{298} of substituted benzenes with the general formula shown in Scheme 1 are given in Table 1. From a qualitative perspective, the trend in binding is what would be predicted based on electrostatic arguments. Electron deficient aromatics, such as **F4**, **CN3**, **NO₂2m**, and **NO₂2p**, exhibit very



Scheme 1 General structure of Na⁺-substituted benzene complexes.

weak cation- π binding, and increasing the number of electron withdrawing substituents on the substituted benzene results in smaller E_{bind} and ΔH_{298} binding values. Conversely, electron-rich aromatics, such as the methyl-, hydroxyl-, amino-, methoxy-, and dimethylamino-substituted benzenes have the strongest cation- π binding. For the most part, increasing the number of electron-donating substituents increases the cation- π binding; however, there are a few exceptions worth noting. The **OH2o** dimer is slightly more binding than would be expected, and this is because the ortho-substitution results in slight rotation of one of the hydroxyl groups, thus allowing the oxygen lone pair to participate in, and enhance, the binding between the aromatic and the cation. The opposite happens with amino-substituted aromatics, and the **NH₂2o** and **NH₂4** dimers are less binding than would be expected. This is also due to substituent rotation, however the result is a hydrogen atom repelling the cation, and decreasing the binding energy. The same result is seen for **N(CH₃)₂2o**.

The correlation between the cation- π ΔH_{298} values and the aromatic $\Sigma\sigma_p$, $\Sigma\sigma_m$, $\Sigma(\sigma_m+\sigma_p)$, or Θ_{zz} values are shown in Figure 1. The correlations are decent, with r^2 values ranging from 0.79 to 0.90, and the $\Sigma(\sigma_m+\sigma_p)$ value gives the best results. The results for the E_{bind} values are almost identical, and the correlation graphs are given in the Supporting Information (SI). The correlations in Figure 1 comparing cation- π binding

Table 1 MP2(full)/6-311++G** Calculated Na⁺-Substituted Benzene Binding Energies (E_{bind}) and Enthalpies (ΔH_{298}).^a

Arene-Na ⁺ Complex	E_{bind} (kcalmol ⁻¹)	ΔH_{298} (kcalmol ⁻¹)	Arene-Na ⁺ Complex	E_{bind} (kcalmol ⁻¹)	ΔH_{298} (kcalmol ⁻¹)
C ₆ H ₆	-21.41	-18.53	NO ₂ 2m	-1.29	-1.89
F1	-17.02	-14.61	NO ₂ 2p	-0.65	-1.32
F2o	-13.07	-10.92	CH ₃ 1	-23.21	-21.33
F2m	-12.87	-11.45	CH ₃ 2o	-24.45	-22.95
F2p	-12.49	-11.16	CH ₃ 2m	-24.68	-23.21
F3	-8.89	-7.72	CH ₃ 2p	-24.79	-23.10
F4	-4.87	-3.27	CH ₃ 3	-26.33	-24.66
Cl1	-17.80	-15.33	CH ₃ 4	-26.87	-25.84
Cl2o	-15.50	-12.76	OH1	-21.22	-18.56
Cl2m	-14.78	-12.45	OH2o	-22.11	-21.02
Cl2p	-14.45	-13.10	OH2m	-21.26	-17.98
Cl3	-11.87	-10.66	OH2p	-21.69	-18.00
Cl4	-7.96	-8.80	OH3	-22.73	-18.83
Br1	-18.00	-15.61	OH4	-21.89	-20.87
Br2o	-15.89	-14.40	NH ₂ 1	-25.37	-24.20
Br2m	-15.41	-13.25	NH ₂ 2o	-26.93	-26.08
Br2p	-15.01	-13.64	NH ₂ 2m	-31.06	-29.76
Br3	-13.19	-10.89	NH ₂ 2p	-29.97	-28.16
Br4	-11.77	-10.71	NH ₂ 3	-35.17	-33.52
I1	-18.51	-16.17	NH ₂ 4	-30.28	-28.95
I2o	-17.14	-15.62	OCH ₃ 1	-23.56	-21.63
I2m	-16.43	-14.30	OCH ₃ 2o	-25.73	-22.55
I2p	-16.05	-14.68	OCH ₃ 2m	-25.59	-23.18
I3	-14.97	-12.73	OCH ₃ 2p	-24.87	-23.17
I4	-14.45	-13.46	OCH ₃ 3	-27.50	-24.57
CN1	-12.19	-11.23	OCH ₃ 4	-28.04	-26.47
CN2o	-4.37	-4.93	N(CH ₃) ₂ 1	-28.36	-26.56
CN2m	-4.28	-2.41	N(CH ₃) ₂ 2o	-28.74	-27.16
CN2p	-3.95	-2.92	N(CH ₃) ₂ 2m	-33.53	-31.81
CN3	2.47	4.36	N(CH ₃) ₂ 2p	-30.72	-29.29
NO ₂ 1	-10.56	-9.84	N(CH ₃) ₂ 3	-39.67	-37.92

^a All E_{bind} values have been corrected for basis set superposition error.

energies to Hammett constants or the aromatic quadrupole moment contain significantly more substituted benzenes than have been investigated in prior studies, and in general this results in correlations that are not as strong as was previously reported.^{9,10,12,15,32} Computational work by Jiang and coworkers showed excellent correlations between cation- π binding enthalpies and $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$ values for seven substituted benzenes, with $r^2 = 0.98$ and 0.99 depending on the cation.³² For the 62 substituted benzenes shown in Table 1, the correlation between the ΔH_{298} values and the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$ values has an $r^2 = 0.90$ (Figure 1a), and while this is the best correlation shown in Figure 1, it cannot reasonably be described as excellent. There are no computational studies describing the correlation between cation- π binding energies and Hammett σ_{p} values; however, Hunter showed an excellent correlation experimentally, via their chemical double-mutant cycles, with three cation- π complexes.¹² Obviously, the correlation between cation- π binding enthalpies and $\Sigma\sigma_{\text{p}}$ values in Figure 1b, with $r^2 = 0.85$, is not excellent. Computational work by Dougherty and coworkers discussed a “rough agreement” between cation- π binding energies and the Hammett σ_{m} value for five mono-substituted benzenes,⁹ and the correlation shown in Figure 1 (c), with $r^2 = 0.83$, would be rightly described as rough. Finally, the correlation between cation- π binding enthalpies and the substituted benzene Θ_{zz} values has $r^2 = 0.79$ (Figure 1d), which is about the same as the correlation previously reported

by Lewis and Clements.¹⁰ It is important to recall that Dougherty showed much better correlations with the aromatic ESPs ($r^2 = 0.98$),⁹ and Suresh with the aromatic MESP ($r^2 > 0.97$).¹⁷ Furthermore, the latter study contained a very large number of substituted benzenes. Still, as stated previously, ESPs and MESP values are calculated values, and it would be preferable to use substituent constants for the prediction of cation- π binding since they don't require calculations before using them. As the work presented here shows, Hammett substituent constants do not suffice to accurately predict cation- π binding strength (ΔH_{298} or E_{bind}). Thus, SAPT calculations were performed to determine what forces are important in the cation- π binding of aromatics, and to aid in the development of an improved parameter for correlating cation- π ΔH_{298} and E_{bind} values.

3.2 SAPT Energy Decomposition Calculations

Symmetry Adapted Perturbation Theory (SAPT) calculations were performed on the following 12 selected substituted benzenes: **OH4**, **NH₂2o**, **N(CH₃)₂1**, **OH2o**, **OCH₃2o**, **CH₃2p**, **C₆H₆**, **F3**, **Cl1**, **CN1**, **CN2m**, and **NO₂2m**. The substituted benzenes were chosen to cover a broad range of Hammett constant values. For instance, the $\Sigma\sigma_{\text{p}}$ range of the 12 substituted benzenes chosen for SAPT calculations is -1.48 to 1.56, and only **NH₂4**, **N(CH₃)₂3**, **NH₂3**, **N(CH₃)₂2o**, **N(CH₃)₂2m**, and **N(CH₃)₂2p** are outside this range on the

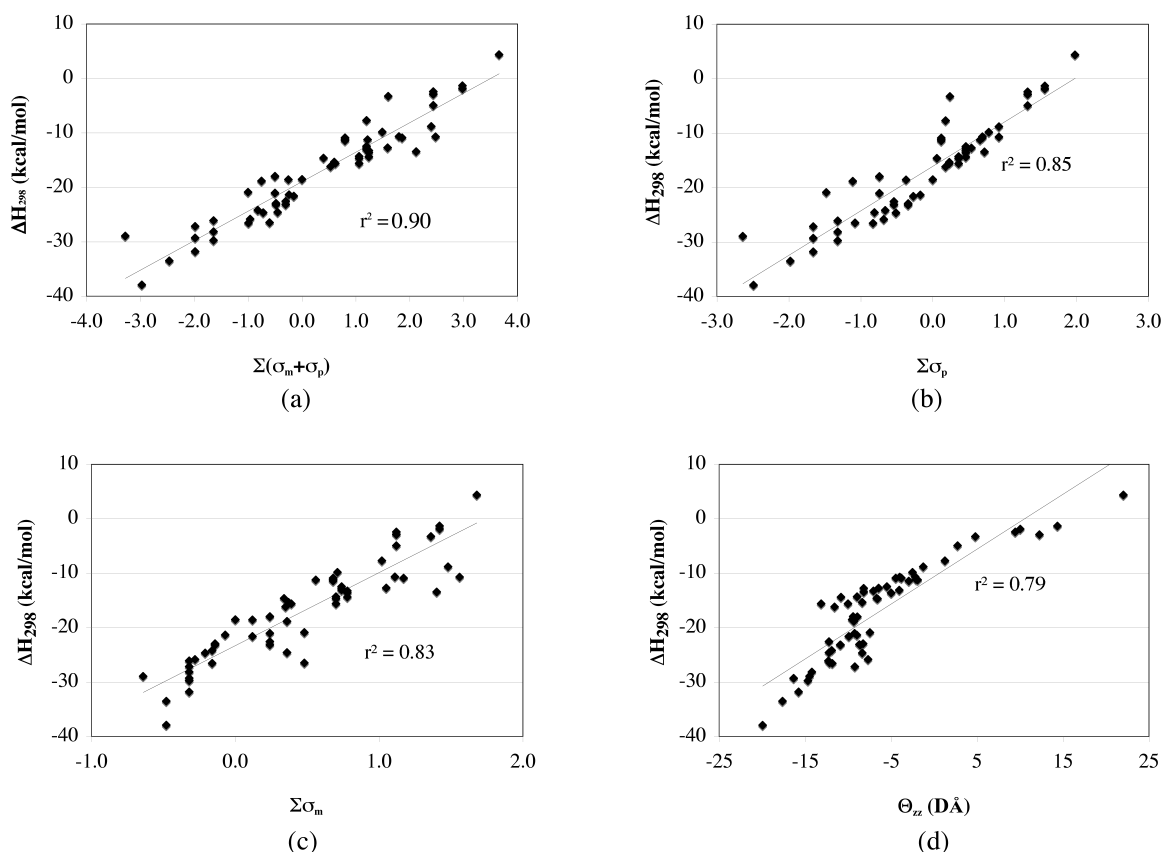


Fig. 1 Correlation between cation- π binding enthalpies (ΔH_{298}) and either (a) $\Sigma(\sigma_m + \sigma_p)$, (b) $\Sigma\sigma_p$, (c) $\Sigma\sigma_m$, or (d) Θ_{zz} , for the substituted benzenes in Table 1.

electron-donating end of the spectrum, while just CN3 is outside the range on the electron-withdrawing end of the spectrum. The chosen aromatics cover a similarly broad range of the $\Sigma(\sigma_m + \sigma_p)$, $\Sigma\sigma_m$, and Θ_{zz} values. The component energies E_{ele} , E_{exch} , E_{ind} , and E_{disp} , and the E_{SAPT} energies for the 12 selected Na^+ -substituted benzene dimers are given in Table 2. Note that the E_{SAPT} energy is the sum of the E_{ele} , E_{exch} , E_{ind} , and E_{disp} energies, and is thus equivalent to the E_{bind} energies in Table 1. Of course, the

E_{bind} energies were determined using the MP2(full)/6-311++G** optimized Na^+ -substituted benzene geometries, with BSSE correction, while the E_{SAPT} energies were determined at the CCSD/6-311++G** level of theory using the MP2(full)/6-311++G** optimized geometries, and thus the E_{bind} and E_{SAPT} numbers differ slightly in absolute value; the mean absolute difference between the E_{bind} and E_{SAPT} values is $1.51 \text{ kcal mol}^{-1}$. More importantly, the relative values are almost identical, with the only difference among

Table 2 SAPT Calculated Component Energies (E_{ele} , E_{exch} , E_{ind} , E_{disp}), in kcal mol^{-1} , for Selected Na^+ -Substituted Benzene Complexes.^a

Na^+ -Arene Complex	E_{ele}	E_{exch}	E_{ind}	E_{disp}	E_{SAPT}
OH4	-15.31	8.47	-16.52	-0.70	-24.06
NH ₂ 2o	-21.52	10.59	-17.53	-0.78	-29.24
N(CH ₃) ₂ 1	-21.54	10.48	-18.10	-0.79	-29.95
OH2o	-15.98	8.98	-15.98	-0.71	-23.68
OCH ₃ 2o	-19.18	10.22	-17.95	-0.77	-27.68
CH ₃ 2p	-18.29	10.29	-17.49	-0.79	-26.28
C ₆ H ₆	-15.39	8.93	-15.29	-0.70	-22.45
F3	-1.64	5.59	-13.62	-0.55	-10.22
Cl1	-10.62	8.19	-15.79	-0.69	-18.91
CN1	-4.15	6.86	-15.30	-0.64	-13.23
CN2m	5.34	4.91	-14.93	-0.56	-5.24
NO ₂ 2m	7.46	4.55	-14.31	-0.54	-2.84

^a SAPT calculations performed at CCSD/6-311++G** level of theory with basis set superposition error correction. Geometries are from the optimized MP2(full)/6-311++G** structures.

the complexes in Table 2 being that **OH2o** has a slightly more binding E_{bind} value than **OH4**, while **OH4** has a slightly more binding E_{SAPT} value. Therefore, we have great confidence that the trends in the component energy data for the 12 selected Na^+ -substituted benzene complexes (Table 2) are representative of the entire set of complexes in Table 1.

The major contributors to the overall cation- π binding energies (E_{bind} or E_{SAPT}) are the E_{ele} and E_{ind} values (Table 2); however, there is much greater variability in the E_{ele} values compared to the E_{ind} values. As a result, sometimes the E_{ele} values are the greatest contributor to the overall cation- π binding strength, and sometimes the E_{ind} values contribute most. For the electron-rich aromatics the E_{ele} component energy either contributes slightly more, or about the same, to the overall binding energy as E_{ind} . In contrast, for the electron-poor aromatics the E_{ind} component energy generally contributes much more to the overall binding strength than the E_{ele} value. In fact, for **CN2m** and **NO22m** the cation- π complexes are binding solely due to induction; the E_{ele} component is repulsive for these two complexes.

Plotting the data for each component energy in Table 2 against the respective $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz} values (Figure 2 (a) – (d)), where the data is always arranged from most negative to most positive $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz}

value, reveals why these parameters do not perform as well as might be expected in predicting cation- π binding energies of substituted benzenes. Although the E_{ele} component varies much more so than the other component energies, the E_{exch} , E_{ind} , and E_{disp} values also vary depending on the aromatic substitution pattern (Figure 2). As would be expected, the variations in the E_{ele} , E_{exch} , E_{ind} , and E_{disp} component energies do not all correlate well with the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, and $\Sigma\sigma_{\text{m}}$ Hammett parameters, and the aromatic Θ_{zz} values. Table 3 shows the correlation coefficients, r^2 , for the correlation between the component energies and either the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz} values, and in each case, except for $\Sigma\sigma_{\text{m}}$, the best correlation is found for E_{ele} . For the $\Sigma\sigma_{\text{m}}$ value the correlation with E_{ele} is still good, but a slightly better correlation is found with E_{exch} . In fact, for the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{m}}$, and Θ_{zz} values the correlations with E_{ele} , E_{exch} , and E_{disp} are always decent to very good, with r^2 values ranging from 0.85 to 0.95. The correlations with E_{ind} are quite poor, and thus it appears the failure of the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{m}}$, and Θ_{zz} values to properly predict the effects of induction ultimately leads to their less than desirable performance in predicting cation- π ΔH_{298} or E_{bind} values (Figure 1 and SI). The $\Sigma\sigma_{\text{p}}$ value does not perform well in predicting any of the component energies (Table 3); the correlation with E_{ele} is best with $r^2 = 0.80$, which makes it surprising that $\Sigma\sigma_{\text{p}}$ values perform decently in predicting

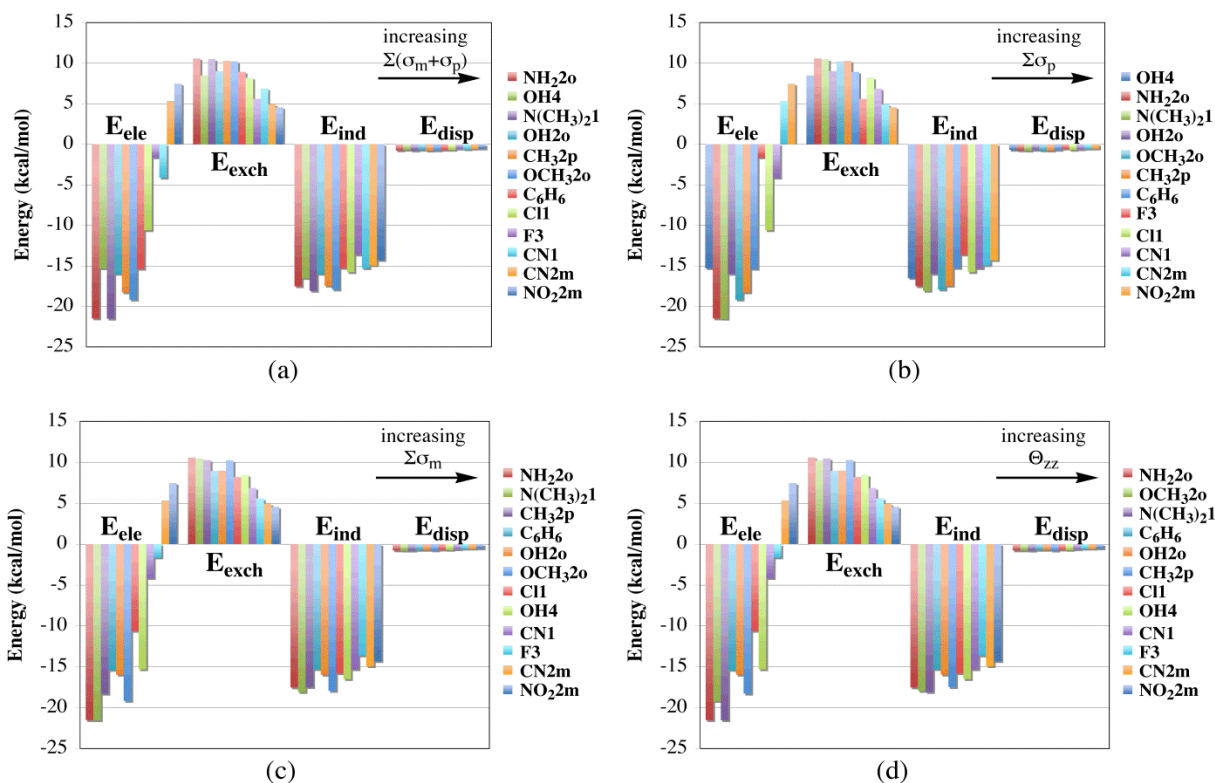


Fig. 2 The SAPT calculated contributions from electrostatics (E_{ele}), exchange (E_{exch}), induction (E_{ind}), and dispersion (E_{disp}) to the overall Na^+ binding energy of **OH4**, **NH22o**, **N(CH3)21**, **OH2o**, **OCH32o**, **CH32p**, **C6H6**, **F3**, **Cl1**, **CN1**, **CN2m**, and **NO22m**. The aromatics are arranged, from left to right, in: (a) increasing $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$ value; (b) increasing $\Sigma\sigma_{\text{p}}$ value; (c) increasing $\Sigma\sigma_{\text{m}}$ value; and (d) increasing Θ_{zz} value.

Table 3 Correlation Coefficients, r^2 , for the Correlation between SAPT Calculated Component Energies (E_{ele} , E_{exch} , E_{ind} , E_{disp}) and $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, Θ_{zz} , or $\Sigma\Pi^+$ values.

Parameter	r^2 with E_{ele}	r^2 with E_{exch}	r^2 with E_{ind}	r^2 with E_{disp}
$\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$	0.94	0.86	0.62	0.86
$\Sigma\sigma_{\text{p}}$	0.80	0.69	0.50	0.62
$\Sigma\sigma_{\text{m}}$	0.90	0.92	0.65	0.89
Θ_{zz}	0.95	0.92	0.60	0.85
$\Sigma\Pi^+$	0.99	0.97	0.75	0.94

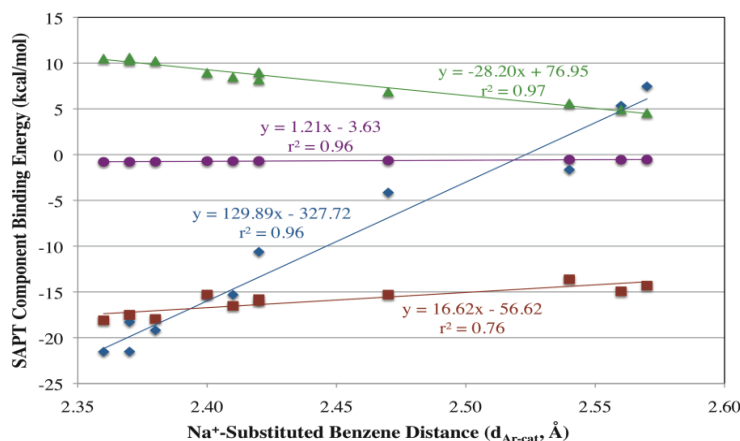
ΔH_{298} or E_{bind} (Figure 1 and SI). Still, from a relative standpoint the correlation between $\Sigma\sigma_{\text{p}}$ and E_{ind} is the worst among the component energies, and it appears safe to say that like the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{m}}$, and Θ_{zz} values, the $\Sigma\sigma_{\text{p}}$ value also does a poor job predicting the effects of induction on cation- π binding. Thus, the less than ideal correlations between the aromatic $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz} values and the cation- π ΔH_{298} or E_{bind} values (Figure 1 and SI) can largely be attributed to the E_{ind} component energies.

3.3 The Correlation between SAPT Component Energies and Cation-Substituted Benzene Distances ($d_{\text{Ar-cat}}$)

Inspection of the Na^+ -substituted benzene ion-arene centroid distance ($d_{\text{Ar-cat}}$), via the lens of the relative component energies, reveals some interesting trends. Figure 3 shows that the E_{ele} , E_{disp} , and E_{exch} component energies all correlate very well with $d_{\text{Ar-cat}}$ with r^2 values of 0.96, 0.96, and 0.97, respectively. In contrast, the correlation between E_{ind} and $d_{\text{Ar-cat}}$ is comparatively poor with an r^2 value of 0.76. This analysis further supports the view that the induction term is primarily responsible for the Na^+ -substituted benzene ΔH_{298}

and E_{bind} values not correlating very well with the aromatic $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, or $\Sigma\sigma_{\text{m}}$ parameters, or with the Θ_{zz} values.

The relationship between the attractive forces governing ion-neutral interactions and the distance between the ion and the neutral molecule are well understood,³³ and the slopes of the lines in Figure 3 are what would be expected. For instance, for classic ion-neutral complexes at long distances, the E_{ele} term should vary as $d_{\text{Ar-cat}}^{-3}$, E_{ind} should vary as $d_{\text{Ar-cat}}^{-4}$, and E_{disp} should vary as $d_{\text{Ar-cat}}^{-6}$. Thus, electrostatics should be most sensitive to changes in $d_{\text{Ar-cat}}$, followed by induction, and then dispersion. An increase in the sensitivity of the component energy towards changes in $d_{\text{Ar-cat}}$ should manifest itself in greater slopes in Figure 3, and this is exactly what is observed. Plotting E_{ele} against $d_{\text{Ar-cat}}$ yields a line with a slope of approximately 130, for E_{ind} the slope is about 17, and for E_{disp} the slope is barely above 1. Note, the relationship between exchange energies and ion-neutral molecule intermolecular distances has not been widely studied.

**Fig. 3** Correlation between Na^+ -substituted benzene distances ($d_{\text{Ar-cat}}$) and E_{ele} (blue diamonds), E_{ind} (red squares), E_{disp} (purple circles), and E_{exch} (green triangles).

3.4 The Cation- π Substituent Constant Π^+

The fact that E_{ind} values correlate so poorly with the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, and Θ_{zz} values (Table 3), and the fact that E_{ind} does not correlate very well with $d_{\text{Ar-cat}}$ (Figure 3), suggests the reason the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, and $\Sigma\sigma_{\text{m}}$ parameters, and the and Θ_{zz} values, do not perform better in predicting cation- π ΔH_{298} and E_{bind} values is because of the energy due to induction. Two approaches were considered for

developing an enhanced method to predict cation- π ΔH_{298} and E_{bind} values: a two-parameter equation, such as the one we employed for substituted benzene-benzene dimers,³⁴ or the development of a new parameter to specifically account for how a cation interacts with substituted aromatics. Taking the latter approach, a cation- π substituent constant, termed Π^+ , was developed using Na^+ -mono-substituted benzene ΔH_{298} values, as shown in Equation 1. Dividing by

Table 4 Cation- π Substituent Constants Π^+ .^a

Substituent	Π^+	Substituent	Π^+
H	0.000	NO ₂	0.275
F	0.103	CH ₃	-0.061
Cl	0.082	OH	-0.001
Br	0.074	OCH ₃	-0.067
I	0.059	NH ₂	-0.116
CN	0.218	N(CH ₃) ₂	-0.156

^a Cation- π substituent constants, Π^+ , calculated using Equation 1.

the Na⁺-C₆H₆ ΔH_{298} value and applying the $-\log$ function yields an H atom Π^+ value of 0.000.

$$\Pi^+ = -\log[(\Delta H_{298}(\text{Na}^+-\text{C}_6\text{H}_5\text{X})) / (\Delta H_{298}(\text{Na}^+-\text{C}_6\text{H}_6))] \quad \text{Eq. 1}$$

The Π^+ values for the substituents used in this study are collected in Table 4, and Figure 4 shows how well the substituent constant performs at predicting the cation- π ΔH_{298} and E_{bind} values from Table 1. Thus, the aromatics included in the correlations in Figures 1 and 4 are the exact same. Of course, $\Sigma\Pi^+$ values were employed since mono- and multi-substituted aromatics were investigated. It is worth noting that the Π^+ parameter, as determined via Equation 1, accounts for how the cation binding of an aromatic increases, or decreases, upon substituting an H atom for a substituent. The $-\log$ function results in electron withdrawing substituents having positive values and electron donating substituents having negative values, in a similar fashion to Hammett constants. The correlations between the E_{ele} , E_{ind} , E_{disp} , and E_{exch} values in Table 2 and the $\Sigma\Pi^+$ parameter are 0.99, 0.75, 0.94, and 0.97, respectively (Table 3). Each correlation is better than the corresponding component energy correlations for the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, and Θ_{zz} values (Table 3) and, importantly, for E_{ind} the correlation is significantly improved, although it is still not great. This explains why the $\Sigma\Pi^+$ values do a much better job at predicting cation- π ΔH_{298} and E_{bind} values than $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz} : Π^+ does a much better a job of taking into account the effects of induction on cation-

π binding, and it also does a better job of taking into account the effects of electrostatics, exchange, and dispersion.

The generality of the Π^+ parameter was examined by using it to correlate the cation- π binding energies of substituted benzenes where the cation is not Na⁺, and where different theoretical methods were employed to calculate the binding strength. A study by Sayyed and Suresh investigated the Li⁺, Na⁺, K⁺, and NH₄⁺ binding of benzene, mono-, para-di-, 1,3,5-tri- and hexa-substituted benzenes where the substituents were N(CH₃)₂, NH₂, CH₃, OH, F, Cl, CN, and NO₂.¹¹ The cation- π binding energies were calculated at the B3LYP/6-311+G(d,p) level of theory, and correlating the E_{bind} value with the $\Sigma\Pi^+$ parameters determined here yields r^2 values of 0.95 for the Li⁺-arene complexes and 0.94 for the Na⁺, K⁺, and NH₄⁺-arene complexes. The Sayyed and Suresh study involved 30 substituted benzenes, and unlike the study we present here they included three hexa-substituted aromatics: hexaamino-, hexamethyl-, and hexafluoro-benzene.¹¹ The hexaamino- and hexamethyl-benzene cation-arene complexes would have the same steric issues discussed above for N(CH₃)₂4 and NO₂20, and this likely explains why they are the primary cause for the correlations not being closer to unity. Omitting the hexaamino- and hexamethyl-benzene cation-arene complexes, the correlations between the Sayyed and Suresh Li⁺, Na⁺, K⁺, and NH₄⁺-substituted benzene binding energies and the $\Sigma\Pi^+$ values have r^2 values of 1.00, 0.99,

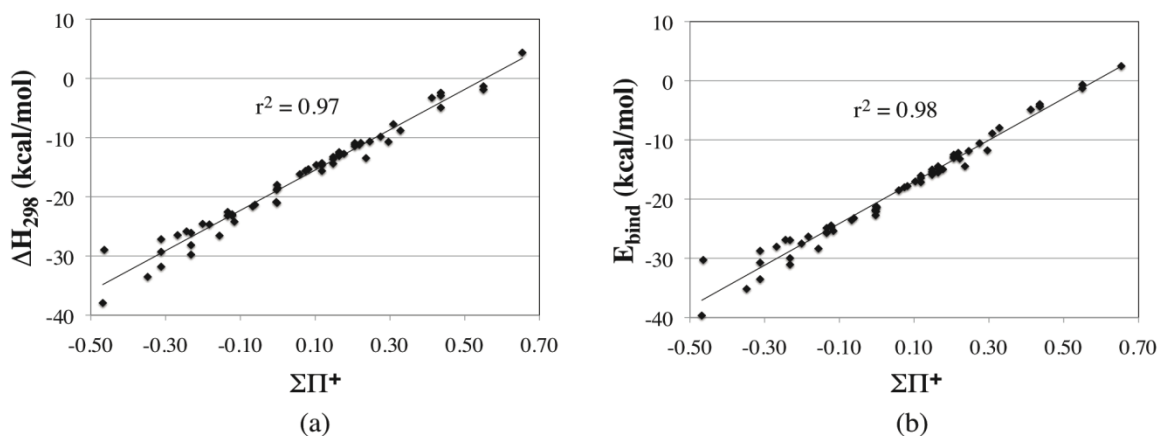


Fig. 4 Correlation between the cation- π substituent constant Π^+ and the cation- π ΔH_{298} (a) or E_{bind} (b) values.

0.98, and 0.98 respectively. In addition to including hexa-substituted aromatics, many of the multi-substituted aromatics in the Sayyed and Suresh study had different substituents. For instance, one of the 1,3,5-substituted aromatics investigated by Sayyed and Suresh was 3-cyano-5-fluoroaniline.¹¹ This is different from the work reported here where all substituted benzenes contain the same substituent. Another study by Sayyed and Suresh reported the Mg⁺ and Cu⁺ binding of benzene and mono-substituted aromatics where the substituents were N(CH₃)₂, NH₂, CH₃, OH, F, Cl, CN, and NO₂,³⁵ and the correlations of the B3LYP/6-311+G(d,p) calculated cation- π binding energies and the Π^+ parameters determined here have r^2 values of 0.99 for the Mg⁺-arene complexes and 0.97 for the Cu⁺-arene complexes. Thus, the Π^+ parameters developed here are general, as they correlate cation- π binding energies calculated with cations other than Na⁺, which was used to derive the parameters, and they correlate cation- π binding energies calculated using a theoretical level and basis set not used to derive the parameters.

The Π^+ parameters perform as well at predicting the relative cation- π binding strength of substituted benzenes as the aromatic MESP values. The study by Suresh and Sayyed, with a large number of substituted benzenes, had correlations between cation- π binding energies and the aromatic MESP values with $r^2 > 0.97$.¹¹ The correlations between the Π^+ values and the cation- π ΔH_{298} and E_{bind} values reported here (Figure 4), also with large numbers of substituted benzenes, have $r^2 = 0.97$ and $r^2 = 0.98$, respectively. This might lead to speculation about a relationship between the Π^+ parameters and aromatic MESP values. While such a relationship may exist, what can safely be said without the requisite thorough investigation is that both the Π^+ parameters and the MESP values directly represent the effects of a substituent on an aromatic π -electron density. Hammett constants, however, directly represent the effect of an aromatic substituent on the ionization of meta- and para-substituted benzoic acids, and the aromatic quadrupole moment is a measure of anisotropy. Thus, it is not surprising that the Π^+ parameters and the MESP values perform so much better than Hammett constants and the quadrupole moment at predicting relative cation- π binding strengths.

4 Conclusions

Cation- π interactions of substituted benzenes have been shown to correlate, to a decent degree, with the aromatic $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz} values (Figure 1). Previous studies had shown better correlations with some of these parameters; however, the current study contains significantly more points. SAPT calculations show the electrostatic (E_{ele}) and induction (E_{ind}) terms are generally the largest contributors to cation- π binding, and that electrostatics is most sensitive to changes in cation-arene distances ($d_{\text{Ar-cat}}$).

SAPT calculations also suggest that E_{ind} is the primary reason for the poorer than expected correlation between cation- π binding (ΔH_{298} or E_{bind}) and the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz} values; these values correlate to a decent degree with the SAPT calculated E_{ele} , E_{exch} , and E_{disp} values, but the correlation with E_{ind} is quite poor (Table 3). Further support that induction is the primary factor contributing to the poor correlation between cation- π ΔH_{298} or E_{bind} values and the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz} values was found in the correlation between the SAPT calculated component energies and Na⁺-substituted benzene ion-arene centroid distances, $d_{\text{Ar-cat}}$ (Figure 3). Due to the inability of the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz} values to accurately predict cation- π ΔH_{298} values a cation- π substituent constant, Π^+ , was developed from Na⁺-mono-substituted benzene binding enthalpies using Equation 1. The Π^+ parameters developed here (Figure 4) physically represent the effect on the strength of cation-substituted benzene binding when an aromatic H atom is replaced by a substituent. The $\Sigma\Pi^+$ values correlate very well with the cation- π ΔH_{298} values, and they correlate better with the SAPT calculated component energies than the Hammett parameters or the Θ_{zz} values (Table 3); the most significant difference between the correlations with the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz} values and the correlation with the $\Sigma\Pi^+$ parameter is for E_{ind} . While the SAPT calculations show that electrostatics are the dominant force in cation- π binding, they also show that the $\Sigma(\sigma_{\text{m}}+\sigma_{\text{p}})$, $\Sigma\sigma_{\text{p}}$, $\Sigma\sigma_{\text{m}}$, or Θ_{zz} values will never accurately predict cation- π ΔH_{298} values due to the induction energy. The Π^+ parameter presented here is superior to $(\sigma_{\text{m}}+\sigma_{\text{p}})$, σ_{p} , σ_{m} , or Θ_{zz} for the accurate prediction of cation- π binding, and it is worth noting that the reason may simply be because these parameters, especially the Hammett parameters, were not developed for such purposes. Hammett constants were derived from the relative rates of ionization of substituted benzoic acids, which have little in common with the non-covalent cation- π binding of aromatics. Parameters specifically derived to describe cation- π binding, as was done here with Π^+ , would reasonably be expected to perform better than Hammett constants at predicting the relative strength of cation- π binding, and that is certainly the result of this work. Importantly, the Π^+ parameter is general, as was demonstrated by using it to correlate the cation- π binding energies of substituted aromatics reported in work performed by other research groups. The correlations between the Π^+ parameters and the cation- π binding energies of cation-arene complexes where the cation was not Na⁺, which was used here to derive the Π^+ values, were excellent. This includes complexes where the cations were Li⁺, K⁺, NH₄⁺, Mg⁺, and Cu⁺.

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6 Notes and references

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