Supporting information

Accurate Prediction of Cation-π Interaction Energy Using Substituent Effects

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Reasons for fixing the intercept equal to the unsubstituted one

The intercept in the E_M^+ and ΔV_{min} has been kept equal to the E_M^+ of unsubstituted complex designated as $E_M^{+\prime}$. In the case of $C_6H_5X\cdots M^+$, the equations corresponding to the best fit lines are

$E_{Li}^+ = 1.072\ \Delta V_{min} - 38.8$ (S1) for Li^+ and correlation coefficient (r) is 0.993

$E_{Na}^+ = 0.840\ \Delta V_{min} - 23.9$ (S2) for Na^+ and $r = 0.995$

$E_K^+ = 0.686\ \Delta V_{min} - 16.5$ (S3) for K^+ and $r = 0.994$

$E_{NH4}^+ = 0.690\ \Delta V_{min} - 16.2$ (S4) for NH_4^+ and $r = 0.987$

It may be noted that the $E_M^{+\prime}$ (interaction energy of the cation with benzene) of $C_6H_5X\cdots Li^+$, $C_6H_5X\cdots Na^+$, $C_6H_5X\cdots K^+$, and $C_6H_5X\cdots NH_4^+$ systems are -37.8 kcal/mol, -23.4 kcal/mol, -15.8 kcal/mol and -15.4 kcal/mol respectively which are very close to the value of the intercept obtained in the equations S1, S2, S3 and S4, respectively. By fixing the $E_M^{+\prime}$ as the intercept in the above mentioned correlation equations, the predicted E_M^+ can be written as

$E_{Li}^+ = 1.026\ \Delta V_{min} - 37.8$ (S5) for Li^+ and $r = 0.986$

$E_{Na}^+ = 0.819\ \Delta V_{min} - 23.4$ (S6) for Na^+ and $r = 0.993$

$E_K^+ = 0.655\ \Delta V_{min} - 15.8$ (S7) for K^+ and $r = 0.985$

$E_{NH4}^+ = 0.655\ \Delta V_{min} - 15.4$ (S8) for NH_4^+ and $r = 0.977$

The predicted value of E_M^+ using these equations (S5 - S8) showed a mean absolute deviation of 0.27 kcal/mol, 0.10 kcal/mol, 0.14 kcal/mol, and 0.26 kcal/mol, for Li^+, Na^+, K^+ and NH_4^+, respectively which means that the use $E_M^{+\prime}$ as intercept does not make any significant change in the performance of these equations. Further, this method will allow us to separate the contribution of the substituent effect on the interaction energy (first term in eqs S5 - S8).

Table S1. $E_M^{+\prime}$ (in kcal/mol) and C_M^+ of various cation-π complexes calculated at the B3LYP/6-311+G(d,p) level.

	$C_6H_6\cdots M^{+\,a}$	
M^+	$E_M^{+\prime}$	C_M^+
Li^+	-37.8	1.007
Na^+	-23.4	0.777
K^+	-15.8	0.655
$BeCl^+$	-87.5	1.802
$MgCl^+$	-55.7	1.294
$CaCl^+$	-35.4	0.968
$TiCl_3^+$	-51.7	1.229
$CrCl_2^{+\,b}$	-58.7	1.341
$NiCl^+$	-76.7	1.630
Cu^+	-49.4	1.193
$ZnCl^+$	-64.1	1.428
NH_4^+	-15.4	0.648
$CH_3NH_3^+$	-13.5	0.617
$N(CH_3)_4^+$	-5.3	0.487
$C(NH_2)_3^+$	-9.8	0.559

[a] C_M^+ is predicted using Eq. (5), [b] Spin multiplicity of Cr is 2.

Table S2. SCF energies (in a.u.) for the cation-π complexes $C_{10}H_7X\cdots M^+$.[a] In parentheses number of imaginary frequencies are also reported.

	$E(C_{10}H_7X)$	$E(C_{10}H_7X\cdots Li^+)$	$E(C_{10}H_7X\cdots Na^+)$	$E(C_{10}H_7X\cdots K^+)$	$E(C_{10}H_7X\cdots NH_4^+)$
$N(CH_3)_2$	-519.987123	-527.344208 (0)	-682.121530 (0)	-1119.782538 (0)	-576.941782 (0)
NH_2	-441.363808	-448.718980 (0)	-603.497120 (0)	-1041.158593 (0)	-498.317757 (0)
CH_3	-425.315358	-432.667304 (0)	-587.445292 (0)	-1025.106483 (0)	-482.265573 (0)
OH	-461.236316	-468.588699 (0)	-623.367024 (0)	-1061.028314 (0)	-518.187653 (0)
H	-385.988889	-393.338395 (0)	-548.117099 (0)	-985.778668 (0)	-442.937757 (0)
F	-485.257234	-492.600879 (0)	-647.380651 (0)	-1085.042921 (0)	-542.202354 (0)
Cl	-845.610477	-852.954747 (0)	-1007.73446 (0)	-1445.396655 (0)	-902.556133 (0)
CN	-478.255446	-485.591495 (0)	-640.372462 (0)	-1078.035560 (0)	-535.194882 (0)
NO_2	-590.546071	-597.879971 (0)	-752.661186 (1)	-1190.324362 (1)	-647.483486 (0)

[a] $E(Li^+)$, $E(Na^+)$, $E(K^+)$, and $E(NH_4^+)$ (in a.u.) are -7.284915, -162.087568, -599.761045 and -56.920320, respectively.

Table S3. SCF energies (in a.u.) for the cation-π complexes $C_8H_6NX\cdots M^+$. [a] In parentheses number of imaginary frequencies are also reported.

	$E(C_8H_6NX)$	$E(C_8H_6NX\cdots Li^+)$	$E(C_8H_6NX\cdots Na^+)$	$E(C_8H_6NX\cdots K^+)$	$E(C_8H_6NX\cdots NH_4^+)$
$N(CH_3)_2$	-497.91201	-505.2749 (0)	-660.050859 (0)	-1097.71094 (0)	-554.87019 (0)
NH_2	-419.28256	-426.64474 (0)	-581.41862 (0)	-1019.0818 (0)	-476.24095 (0)
CH_3	-403.24201	-410.6021 (0)	-565.378172 (0)	-1003.03821 (0)	-460.19746 (0)
OH	-439.15206	-446.51117 (0)	-601.288111 (0)	-1038.94859 (0)	-496.10774 (0)
H	-363.91393	-371.27169 (0)	-526.048484 (0)	-963.708951 (0)	-420.86823 (0)
F	-463.17337	-470.52398 (0)	-625.302112 (0)	-1062.96339 (0)	-520.12259 (0)
Cl	-823.53338	-830.88479 (0)	-985.662732 (0)	-1423.32395 (0)	-880.48308 (0)
CN	-456.18491	-463.52641 (0)	-618.305958 (0)	-1055.96821 (0)	-513.12731 (0)
NO_2	-568.47995	-575.81874 (0)	-730.599026 (0)	-1168.26132 (0)	-625.4206 (0)

[a] $E(Li^+)$, $E(Na^+)$, $E(K^+)$, and $E(NH_4^+)$ (in a.u.) are -7.284915, -162.087568, -599.761045 and -56.920320, respectively.

Table S4. SCF energies of (in a.u.) for the cation-π complexes between Li^+ and the π-systems **1-15**. In parentheses number of imaginary frequencies are also reported.

X	Φ	$E(Li^+)$	E(Φ-X)	E(Φ-X···Li^+)
NH_2	**1**	-7.284915	-189.361714	-196.723326 (0)
CH_3		-7.284915	-157.274531	-164.602273 (0)
F		-7.284915	-277.141453	-[a]
CN		-7.284915	-263.144289	-[a]
NH_2	**2**	-7.284915	-188.095769	-195.456331 (0)
CH_3		-7.284915	-156.026768	-163.359429 (0)
F		-7.284915	-275.834894	-283.135637 (0)
CN		-7.284915	-261.886405	-269.170738 (0)
NH_2	**3**	-7.284915	-344.224844	-351.588736 (0)
CH_3		-7.284915	-312.127070	-319.471523 (0)
F		-7.284915	-432.001398	-439.327431 (0)
CN		-7.284915	-418.005669	-425.310750 (0)
NH_2	**4**	-7.284915	-552.111408	-405.815400 (0)
CH_3		-7.284915	-503.969471	-357.651168 (0)
F		-7.284915	-683.791705	-537.431141 (0)
CN		-7.284915	-662.779508	-516.388026 (0)
NH_2	**5**	-7.284915	-552.111408	-559.481960 (0)
CH_3		-7.284915	-503.969471	-511.328576 (0)
F		-7.284915	-683.791705	-691.120331 (0)
CN		-7.284915	-662.779508	-670.082628 (0)
NH_2	**6**	-7.284915	-530.031807	-537.404487 (0)
CH_3		-7.284915	-481.895244	-489.261404 (0)
F		-7.284915	-661.703624	-669.037567 (0)
CN		-7.284915	-640.709530	-648.017809 (0)
NH_2	**7**	-7.284915	-431.713096	-439.081688 (0)
CH_3		-7.284915	-367.541851	-374.907653 (0)
F		-7.284915	-607.253592	-614.565922 (0)
CN		-7.284915	-579.275934	-[a]
Phe	**8**	-7.284915	-554.960162	-562.313070 (0)
Trp	**9**	-7.284915	-686.561637	-693.918552 (0)
Tyr	**10**	-7.284915	-630.207408	-637.560349 (0)
NH_2	**11**	-7.284915	-552.075630	-559.464746 (0)
CH_3		-7.284915	-503.913144	-511.282740 (0)
F		-7.284915	-683.744749	-691.089000 (0)
CN		-7.284915	-662.714410	-670.034095 (0)
NH_2	**12**	-7.284915	-837.417239	-844.790610 (0)
CH_3		-7.284915	-773.224445	-780.585157 (0)

F		-7.284915	-1012.987384	-1020.316325 (0)
CN		-7.284915	-984.967800	-992.269483 (0)
NH_2	**13**	-7.284915	-1143.199928	-1150.587925 (0)
CH_3		-7.284915	-1078.974982	-1086.352984 (0)
F		-7.284915	-1318.751895	-1326.106289 (0)
CN		-7.284915	-1290.736876	-1298.071797 (0)
NH_2	**14**	-7.284915	-1045.202575	-1052.582321 (0)
CH_3		-7.284915	-964.959048	-972.324020 (0)
F		-7.284915	-1264.657904	-1271.989132 (0)
CN		-7.284915	-1229.636339	-1236.938514 (0)
NH_2	**15**	-7.284915	-1045.202575	-1052.582737 (0)
CH_3		-7.284915	-964.959048	-972.320441 (0)
F		-7.284915	-1264.657904	-1271.982260 (0)
CN		-7.284915	-1229.636339	-1236.931114 (0)

[a]Cation directly interacting with substituent.

Table S5. SCF energies (in a.u.) for the cation-π complexes $C_6H_5X\cdots M^+$. In parentheses number of imaginary frequencies are also reported.

M^+	X	$E(C_6H_5X)$	$E(M^+)$	$E(C_6H_5X\cdots M^+)$
Li^+	OH	-307.558631	-7.284915	-314.904739 (0)
Na^+	H	-232.311246	-162.087568	-394.436132 (0)
K^+	SCH_3	-669.848424	-599.761045	-1269.638064 (0)
$BeCl^+$	SH	-630.525261	-474.665186	-1105.331974 (0)
$MgCl^+$	CCH	-308.477249	-660.081084	-968.645141 (0)
$CaCl^+$	F	-331.580112	-1137.666595	-1469.293906 (0)
$TiCl_3^+$	Cl	-691.934215	-2230.010903	-2922.019062 (0)
$CrCl_2^+$	COOH	-420.948152	-1964.626758	-2385.656607 (0)
$NiCl^+$	CF_3	-569.460851	-1968.147154	-2537.719531 (0)
Cu^+	CN	-324.577761	-1640.176897	-1964.815890 (0)
$ZnCl^+$	NO_2	-436.874621	-2239.260674	-2676.211823 (0)
$NH4^+$	$N(CH_3)_2$	-366.314051	-56.920320	-423.269981 (0)
$CH_3NH_3^+$	NH_2	-287.687628	-96.248988	-383.965861 (0)
NMe_4^+	OCH_3	-346.867565	-214.223199	-561.102047 (0)
$C(NH_2)_3^+$	CH_3	-271.638813	-205.835549	-477.491691 (0)

Table S6. SCF energies (in a.u.) for the cation-π complexes $C_{10}H_7X\cdots M^+$. In parentheses number of imaginary frequencies are also reported.

M^+	X	$E(C_{10}H_7X)$	$E(M^+)$	$E(C_{10}H_7X\cdots M^+)$
Li^+	OH	-461.2363158	-7.2849152	-468.5886993 (0)
Na^+	H	-385.9888892	-162.0875682	-548.1170994 (0)
K^+	SCH_3	-823.5243801	-599.761045	-1423.317368 (0)
$BeCl^+$	SH	-784.2013132	-474.6651857	-1259.014493 (0)
$MgCl^+$	CHO	-499.3445603	-660.0810839	-1159.516454 (0)
$CaCl^+$	CF_3	-723.1354393	-1137.666595	-1860.857341 (0)
$TiCl_3^+$	CN	-478.2554464	-2230.010903	-2708.341577 (0)
$CrCl_2^+$	NO_2	-590.5460711	-1964.626758	-[a]
$NiCl^+$	NH_2	-441.3638078	-1968.147154	-2409.675495 (0)
Cu^+	OCH_3	-500.5454365	-1640.176897	-2140.816196 (0)
$ZnCl^+$	CH_3	-425.3153584	-2239.260674	-2664.691744 (0)
$NH4^+$	CCH	-462.1546042	-56.9203203	-519.1028601 (0)
$CH_3NH_3^+$	F	-485.2572337	-96.24898759	-581.5276358 (0)
NMe_4^+	Cl	-845.6104769	-214.2231994	-1059.84325 (0)
$C(NH_2)_3^+$	COOH	-574.6208178	-205.8355489	-[a]

[a] cation interacting with the substituent.

Table S7. SCF energies (in a.u.) for the cation-π complexes $C_8H_6NX\cdots M^+$. In parentheses number of imaginary frequencies are also reported.

M^+	X	$E(C_8H_6NX)$	$E(M^+)$	$E(C_8H_6NX\cdots M^+)$
Li^+	CCH	-440.0828061	-7.2849152	-447.4369244 (0)
Na^+	F	-463.1733691	-162.0875682	-625.3021121 (0)
K^+	Cl	-823.533382	-599.761045	-1423.323948 (0)
$BeCl^+$	COOH	-552.5554806	-474.6651857	-1027.37192 (0)
$MgCl^+$	$N(CH_3)_2$	-497.9120059	-660.0810839	-1158.108113 (0)
$CaCl^+$	NH_2	-419.2825626	-1137.666595	-1557.027055 (0)
$TiCl_3^+$	OCH_3	-478.4575177	-2230.010903	-2708.584182 (0)
$CrCl_2^+$	CH_3	-403.2420138	-1964.626758	-2367.986533 (0)
$NiCl^+$	CF_3	-701.0663909	-1968.147154	-2669.353613 (0)
Cu^+	CN	-456.1849142	-1640.176897	-2096.443519

				(0)
$ZnCl^+$	NO_2	-568.4799488	-2239.260674	-[a]
$NH4^+$	OH	-439.1520621	-56.9203203	-496.1076677 (0)
$CH_3NH_3^+$	H	-363.9139331	-96.24898759	-460.1927884 (0)
NMe_4^+	SCH_3	-801.4434421	-214.2231994	-1015.688678 (0)
$C(NH_2)_3^+$	SH	-762.1249704	-205.8355489	-[a]

[a]Cation interacting with the substituent.

Table S8. SCF energies (in a.u.) of $C_6H_6\cdots M^+\cdots C_6H_5X$ complexes. In parentheses number of imaginary frequencies are also reported.

X	Li^+	Na^+	K^+
NH_2	-527.386226 (0)	-682.158834 (0)	-1119.812261 (0)
CH_3	-511.332257 (0)	-666.105099 (0)	-1103.758795 (0)
H	-472.001491 (0)	-626.775012 (0)	-1064.429165 (0)
F	-571.263616 (0)	-726.037631 (0)	-1163.692801 (0)
CN	-564.252909 (0)	-719.028050 (0)	-1156.684555 (1)