Supporting Information

Explicit Representation of Cation-π Interactions in Force Fields with $1/r^4$ Non-bonded Terms

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Computational Methods – DFT Calculations

The Gaussian16 package[1] was used for the ab initio and DFT calculations for the cation-π complexes. Geometry optimizations were carried out with B3LYP/6–311 ++ G(d, p) followed by rigid PES scans with ωB97X-D/6-311++G(d,p).[2-3] The distance between the cation center and ring center was scanned at 0.1 Å intervals. Counterpoise correction[5,6] was used to offset basis set superposition errors (BSSE) for all interaction energies.

Table S1. *Ab initio* and DFT Interaction Energies for the Benzene - K^+ Complex

Method	Basis Set	ΔE (kcal/mol)	Ref [a]
CCSD(T)	6-31G(d,p)	-15.0	
MP2	6-311G+(d,p)	-13.5	
MP2	6-311G++(d,p)	-16.6	
MP2	6-311G++(2df, 2pd)	-18.0	
MP2	6-311G++(3df, 3pd)	-18.8	
ωB97X-D	6-311G++(d,p)	-18.2	
ωB97X-D	6-311G++(2df, 2pd)	-18.4	
ωB97X-D	6-311G++(3df, 3pd)	-19.0	
CCSD(T)	CBS	-20.1	Feller[7]
MP2	aug-cc-pVDZ	-18.6	
MP2	aug-cc-pVTZ	-19.7	
MP2	aug-cc-pVQZ	-20.4	
MP2	CBS	-20.8	
CCSD(T)	def2-TZVPPD	-16.9	Ferretti[8]
ωB97X-D	def2-TZVPPD	-17.9	
M062X	def2-TZVPPD	-19.3	
PBE0	def2-TZVPPD	-16.5	
B3LYP	def2-TZVPPD	-15.6	
M06	6-311G++(d,p)	-16.3	Davis[9]
M06	6-31G++(d,p)	-20.3	
CCSD(T)	6-311G++(2d,2p)	-16.5	Marshall[10]
B3LYP	6-31G(d,p)	-15.5	Reddy[11]
B3LYP	6-311G++(d,p)	-15.2	

[a] This work except as noted.

Table S2. Calculated and Experimental Interaction Energies (kcal/mol) at 0 K

Cation-benzene	Exp[a]	ωB97X-D/ 6-311++G(d,p)	CCSD(T)/ CBS[b]	MP2(full)/ 6-311+G(2d,2p)[a]
Li^+	-38.5 ± 3.2	-38.2	-36.1	-34.2
Na^+	-22.1 ± 1.4	-24.7	-24.4	-21.4
K^+	-17.5 ± 0.9	-18.3	-20.0	-17.1
NH_4^+	-19.3[c]	-18.8	-21.4[d]	-18.6
Rb^+	-16.4 ± 0.9	-13.3	-16.3	-12.7
Cs^+	-15.4 ± 1.1	-11.6	-12.4	-11.4

[a] Ref 12. [b] Ref 7. [c] Ref 13, at 298 K. [d] Ref 14.

Table S3. OPLS/2020 Non-Bonded Parameters for Cations[a]

atom	q (e^-)	σ (Å)	ε (kcal/mol)	κ
Li^+	1.0	2.87	0.0005	0.45
Na^+	1.0	4.07	0.0005	0.70
K^+	1.0	5.17	0.0005	0.95
Rb^+	1.0	5.60	0.0005	0.70
Cs^+	1.0	6.20	0.0005	0.75
NH_4^+ - N	-0.40	3.48	0.290	1.00
NH_4^+ - H	0.35	0.0	0.0	0.0
$MeNH_3^+$ - N	-0.30	3.48	0.290	1.00
$MeNH_3^+$ - H_N	0.33	0.0	0.0	0.0
$MeNH_3^+$ - C	0.13	3.50	0.066	0.0
$MeNH_3^+$ - H_C	0.06	2.50	0.030	0.0
Me_4N+ - N	0.0	3.48	0.290	1.00
Me_4N+ - C	-0.05	3.50	0.066	0.0
Me_4N+ - H_C	0.10	2.50	0.030	0.0
Gdm^+ - N	-0.80	3.25	0.170	0.25
Gdm^+ - H	0.46	0.0	0.0	0.0
Gdm^+ - C	0.64	3.55	0.050	0.0
$MeGdm^+$ - N_{Me}	-0.70	3.25	0.170	0.25
$MeGdm^+$ - H_{NMe}	0.44	0.0	0..0	0.0
$MeGdm^+$ - C_{Me}	0.20	3.50	0.066	0.0
$MeGdm^+$ - H_{Me}	0.06	2.50	0.030	0.0

[a] From Refs. 15-17 and the present work.

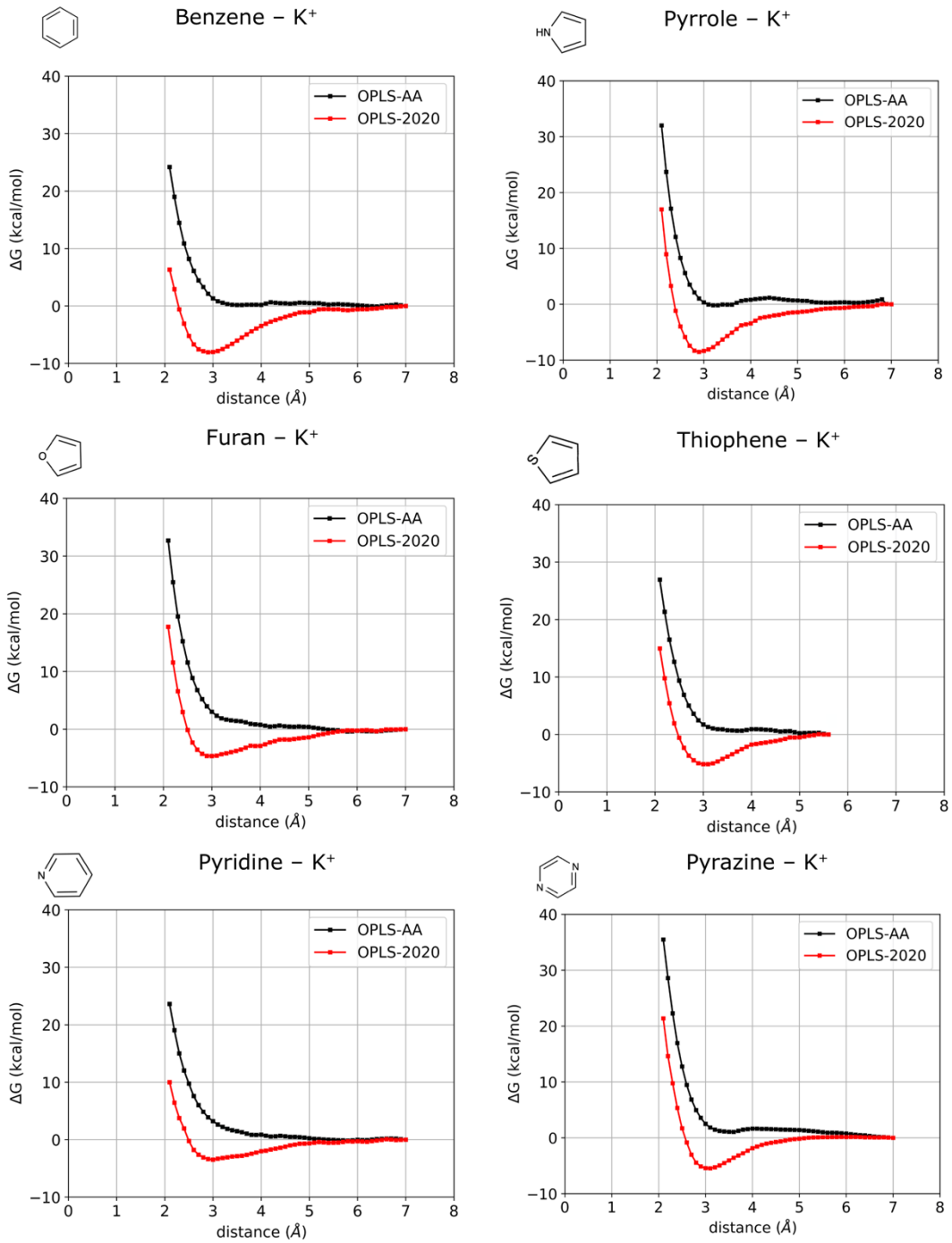

Figure S1. Pmfs for the interaction of K^+ with benzene and heterocycles using OPLS-AA (black) or OPLS/2020 (red), which includes the $1/r^4$ terms for cation-π interactions.

Cartesian Coordinates of the Complexes In Figure 2

	(A)Benzene-NH_4^+ (bidendate)				(B) Benzene-NH_4^+ (monodendate)		
C	-1.2	0	-0.709	C	-1.2	0	-0.709
C	-1.214	0	0.684	C	-1.214	0	0.684
C	-0.014	0	1.393	C	-0.014	0	1.393
C	1.2	0	0.709	C	1.2	0	0.709
C	1.214	0	-0.684	C	1.214	0	-0.684
C	0.014	0	-1.393	C	0.014	0	-1.393
H	-2.158	0	1.217	H	-2.158	0	1.217
H	-0.025	0	2.477	H	-0.025	0	2.477
H	2.133	0	1.26	H	2.133	0	1.26
H	2.158	0	-1.217	H	2.158	0	-1.217
H	0.025	0	-2.477	H	0.025	0	-2.477
H	-2.132	0	-1.26	H	-2.132	0	-1.26
N	0	-2.9	0	N	0	-3	0
H	0.412	-3.493	0.73	H	0.833	-3.342	0.492
H	-0.412	-3.493	-0.73	H	0.01	-3.342	-0.968
H	-0.73	-2.307	0.412	H	-0.843	-3.342	0.475
H	0.73	-2.307	-0.412	H	0	-1.973	0

	(C) Indole-NH_4^+ π6				(D) Indole-NH_4^+ π5		
C	0	0	0	C	0	0	0
C	0	0	1.434	C	0	0	1.434
C	1.19	0	2.185	C	1.19	0	2.185
C	2.393	-0.117	1.483	C	2.393	-0.117	1.483
C	2.415	-0.167	0.064	C	2.415	-0.167	0.064
C	1.234	-0.149	-0.678	C	1.234	-0.149	-0.678
C	-1.37	0.029	-0.418	C	-1.37	0.029	-0.418
C	-2.137	0.069	0.73	C	-2.137	0.069	0.73
H	1.177	-0.011	3.272	H	1.177	-0.011	3.272
H	3.328	-0.172	2.034	H	3.328	-0.172	2.034
H	3.366	-0.309	-0.444	H	3.366	-0.309	-0.444
H	1.26	-0.229	-1.763	H	1.26	-0.229	-1.763
H	-1.751	0	-1.43	H	-1.751	0	-1.43
H	-1.633	-0.002	2.793	H	-1.633	-0.002	2.793
N	-1.312	0.08	1.838	N	-1.312	0.08	1.838
H	-3.212	0.08	0.848	H	-3.212	0.08	0.848
N	1.025	-2.062	0.846	N	-1.015	-1.963	0.747
H	0.543	-2.397	0.024	H	-0.078	-2.326	0.642
H	0.498	-2.312	1.671	H	-1.592	-2.297	-0.012
H	1.116	-1.057	0.796	H	-0.989	-0.954	0.732
H	1.943	-2.481	0.893	H	-1.401	-2.277	1.626

	(E) Benzene-TMA$^+$				(F) Benzene-Gdm$^+$ (T-shaped)		
C	0.005	-0.476	1.332	C	0	0	0
C	0.001	-1.392	0.254	C	0	0	1.395
C	0.003	0.916	1.078	C	1.208	0	2.092
C	-0.003	-0.916	-1.078	C	2.416	0	1.395
C	-0.002	1.392	-0.254	C	2.416	0	0
C	-0.005	0.476	-1.332	C	1.208	0	-0.697
H	0.048	-0.843	2.359	H	-0.952	0	-0.55
H	0.042	-2.465	0.45	H	-0.952	0	1.945
H	0.046	1.622	1.909	H	1.208	0	3.192
H	0.034	-1.622	-1.91	H	3.368	0	1.945
H	0.037	2.465	-0.45	H	3.368	0	-0.55
H	0.031	0.842	-2.36	H	1.208	0	-1.797
N	-4.424	-0.003	0	C	1.415	-4.031	0.827
C	-5.952	-0.007	0.004	N	1.531	-5.354	0.782
C	-3.914	1.099	-0.931	N	0.788	-3.429	1.833
H	-6.296	-0.8	0.674	N	1.92	-3.262	-0.131
H	-6.301	0.968	0.357	H	1.147	-5.93	1.509
H	-6.302	-0.191	-1.016	H	2.005	-5.809	0.022
H	-2.82	1.085	-0.916	H	0.7	-2.429	1.867
H	-4.293	2.059	-0.567	H	0.386	-3.958	2.586
H	-4.29	0.899	-1.939	H	2.404	-3.659	-0.916
C	-3.908	-1.359	-0.49	H	1.832	-2.262	-0.097
C	-3.906	0.253	1.418				
H	-2.814	-1.334	-0.484				
H	-4.285	-1.525	-1.503				
H	-4.28	-2.134	0.187				
H	-2.812	0.251	1.391				
H	-4.278	-0.544	2.069				
H	-4.283	1.224	1.751				

(G) Benzene-Gdm$^+$ (Stacked)				Indole-Gdm$^+$ π6 (Stacked)			
C	0	1.4	0	C	0	0	0
C	0	0.695	-1.22	C	0	0	1.434
C	0	0.694	1.219	C	1.19	0	2.185
C	0.002	-0.714	-1.223	C	2.393	-0.117	1.483
C	0.001	-0.716	1.218	C	2.415	-0.167	0.064
C	0.001	-1.419	-0.003	C	1.234	-0.149	-0.678
H	-0.039	2.48	0.001	C	-1.37	0.029	-0.418
H	-0.039	1.236	-2.156	C	-2.137	0.069	0.73
H	-0.039	1.233	2.156	H	1.177	-0.011	3.272
H	-0.037	-1.253	-2.159	H	3.328	-0.172	2.034
H	-0.037	-1.256	2.153	H	3.366	-0.309	-0.444
H	-0.037	-2.5	-0.004	H	1.26	-0.229	-1.763
C	3.526	0	0.005	H	-1.751	0	-1.43
N	3.535	0.678	-1.146	H	-1.633	-0.002	2.793
H	3.503	0.216	-2.046	N	-1.312	0.08	1.838
H	3.516	1.689	-1.179	H	-3.212	0.08	0.848
N	3.547	0.658	1.167	C	1.352	2.422	0.662
H	3.529	1.668	1.217	N	0.198	2.512	1.315
H	3.525	0.18	2.059	H	-0.677	2.547	0.822
N	3.53	-1.336	-0.007	H	0.169	2.546	2.318
H	3.507	-1.884	0.844	N	2.496	2.381	1.338
H	3.497	-1.869	-0.866	H	2.509	2.419	2.342
				H	3.378	2.31	0.863
				N	1.363	2.373	-0.665
				H	2.225	2.308	-1.177
				H	0.509	2.401	-1.194

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