Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

A Through-Space Description of Substituent Effects Leads to Inaccurate Molecular Electrostatic Potentials and Cation···π Interactions in Extended Aromatic Systems

Enrique M. Cabaleiro-Lago[a,*] and Jesús Rodríguez-Otero[b]

[a] Facultade de Ciencias (Dpto. de Química Física), Universidade de Santiago de Compostela, Campus de Lugo. Avda. Alfonso X El Sabio s/n 27002 Lugo, Galicia (Spain)

[b] Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Física, Universidade de Santiago de Compostela. 15782 Santiago de Compostela (Spain)

Complete references 18 and 23:

18. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. M. J. A, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, 2009.

23. H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, D. P. O'Neill, P. Palmieri, D. Peng, K. P. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson and M. Wang, *Molpro version 2012.1, a package of ab initio programs, see* http://www.molpro.net.

In order to obtain Hodgkin similarity indexes, points from isodensity surfaces between 0.0018 to 0.0022 a.u. were selected, and the index computed as:

$$H = \frac{2\sum_{i=1}^{N}\varphi_{i,A}\varphi_{i,B}}{\sum_{i=1}^{N}(\varphi_{i,A})^2\sum_{i=1}^{N}(\varphi_{i,B})^2}$$

Furthermore, the index was dissected in π and σ contributions, considering that points between 2 and 5 bohr above and below the molecular plane contribute to the π component and points between 0 to 2 bohr above and below the molecular plane contribute to the σ component. The results indicate that changes of MEP due to substitution are more important in the π cloud region.

Table S1. Hodgkin similarity index comparing the true MEPs and those calculated with an additive model. π and σ correspond to a partition including out of plane or in-plane points (π: points between 2 to 5 bohr above and below molecular plane; σ: 0 to 2 bohr).

BENZENE	**total**	**π**	**σ**
NO_2	0.90	0.79	0.95
CN	0.94	0.85	0.96
F	0.97	0.86	1.00
CH_3	0.99	0.98	0.99
OH	0.96	0.88	0.98
NH_2	0.93	0.89	0.96
NAPHTHALENE	**total**	**π**	**σ**
NO_2	0.88	0.71	0.95
CN	0.93	0.80	0.96
F	0.98	0.90	1.00
CH_3	0.99	0.98	1.00
OH	0.97	0.92	0.99
NH_2	0.93	0.89	0.96
ANTHRACENE	**total**	**π**	**σ**
NO_2	0.88	0.67	0.95
CN	0.92	0.79	0.96
F	0.98	0.93	1.00
CH_3	0.99	0.98	1.00
OH	0.97	0.93	0.99
NH_2	0.93	0.89	0.97

Hodgkin index for each ring of anthracene obtained as commented above, considering only regions 2.4 bohr each side of the ring center. It can be observed that the description of the σ component shows similar quality in the three rings, while the π region slightly deteriorates for the rings further apart in NO_2 and CN derivatives. The results suggest the presence of non-local effects that probably act on the whole molecule through changes in its electron cloud.

Table S2. Hodgkin similarity index for anthracene derivatives comparing the true MEPs and those calculated with an additive model. π and σ correspond to a partition including out of plane or in-plane points (π: points between 2 to 5 bohr above and below molecular plane: σ 0 to 2 bohr). Ring 1 is closest to the substituent. Ring regions are defined by considering 2.4 bohr to each side of the ring center following the longitudinal axis of the molecule.

		π			σ			**Total**	
	Ring1	**Ring2**	**Ring3**	**Ring1**	**Ring2**	**Ring3**	**Ring1**	**Ring2**	**Ring3**
NO_2	0.70	0.68	0.60	0.98	0.98	0.97	0.92	0.93	0.89
CN	0.81	0.81	0.74	0.99	0.99	0.98	0.96	0.96	0.92
F	0.64	0.96	1.00	1.00	1.00	1.00	0.93	0.99	1.00
CH_3	0.99	0.99	0.99	1.00	1.00	1.00	0.99	1.00	1.00
OH	0.91	0.95	0.98	0.99	1.00	0.99	0.96	0.97	0.99
NH_2	0.93	0.92	0.94	0.99	0.97	0.97	0.96	0.94	0.95

Table S3. MEPs in kcal mol^{-1} at 2.4 Å over the ring centers of benzene, naphthalene and anthracene as obtained from PBE0/aug-cc-pVDZ calculations and the additive model.

	MEP	**MEP$_{mod}$**	***%dev1***^{a}	***%dev2***^{b}	**MEP**	**MEP$_{mod}$**	**%dev1**^{a}	**%dev2**^{b}
		NO$_2$				**CN**		
Bz	-1.27	-1.51	*-1.9*	*1.7*	-2.57	-3.23	-5.7	4.7
Naph-r1	-1.91	-0.37	*13.8*	*-11.8*	-3.05	-2.11	9.4	-7.2
Naph-r2	-2.94	-7.19	*-42.1*	*32.6*	-3.96	-7.46	-38.6	26.9
Ant-r1	-2.43	0.24	*26.7*	*-21.5*	-3.43	-1.51	21.4	-15.5
Ant-r2	-3.02	-6.40	*-36.6*	*27.6*	-4.02	-6.68	-32.3	21.7
Ant-r3	-4.33	-9.46	*-63.4*	*41.3*	-5.29	-9.46	-58.5	33.6
		CH$_3$				**F**		
Bz	-14.69	-14.43	*-48.1*	*-1.8*	-9.97	-6.23	89.5	-26.4
Naph-r1	-13.36	-13.30	*-18.2*	*-0.5*	-9.11	-5.10	102.3	-30.8
Naph-r2	-14.18	-13.13	*-91.3*	*-8.1*	-10.40	-8.95	55.1	-11.1
Ant-r1	-12.58	-12.70	*75.0*	*1.0*	-8.68	-4.50	111.8	-33.7
Ant-r2	-13.29	-12.35	*-90.4*	*-7.7*	-9.84	-8.17	69.3	-13.6
Ant-r3	-13.50	-12.47	*-95.4*	*-8.3*	-10.57	-10.34	12.4	-1.9
		OH				**NH$_2$**		
Bz	-13.83	-10.42	*1065.6*	*-24.1*	-18.14	-15.87	-56.9	-16.0
Naph-r1	-12.29	-9.25	*410.8*	*-23.3*	-16.18	-14.76	-45.1	-10.9
Naph-r2	-14.04	-11.26	*-275.2*	*-21.3*	-16.84	-13.01	-100.5	-29.4
Ant-r1	-11.44	-8.63	*286.7*	*-22.6*	-15.05	-14.16	-33.8	-7.2
Ant-r2	-13.14	-10.46	*-301.1*	*-21.9*	-15.77	-12.22	-100.9	-29.0
Ant-r3	-13.55	-11.64	*-169.0*	*-15.4*	-15.75	-12.32	-103.0	-27.6

a) Relative to the change on MEP upon substitution.

b) Relative to the MEP of the unsubstituted system. Bz: -14.15 kcal mol^{-1}; Naph: -13.03 kcal mol^{-1}; Ant-r1: -12.42 kcal mol^{-1}; Ant-r2: -12.25 kcal mol^{-1}.

Details of SAPT(DFT) calculations: SAPT(DFT) calculations were performed with Molpro2012. For these calculations, the PBE0 functional was used involving a shift parameter obtained as the sum of the ionization potential and the energy of the highest occupied molecular orbital. Orbital energies and ionization potentials have been obtained by using the PBE functional with the aug-cc-pVDZ basis set. The DFT-SAPT calculations were performed with the aug-cc-pVDZ basis set, using the cc-pVTZ/JKFIT for Hartree–Fock and aug-cc-pVDZ/MP2FIT for the second-order dispersion terms. JKFIT auxiliary basis set for Na has been generated with the AutoAux option of ORCA (F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73-78):

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Table S4. Interaction energy decomposition at the minima of the complexes with sodium cation over the center of the rings of benzene and naphthalene, obtained by interpolation from values along lines passing through ring centers. SAPT(DFT) values with PBE0/aug-cc-pVDZ.

		R_{min} (Å)	**Total**	**Elec**	**Rep**	**Ind**	**Disp**
Bz	H	2.428	-22.29	-15.00	7.86	-14.75	-0.41
	NO_2	2.476	-10.94	-1.83	6.38	-15.10	-0.40
	CN	2.467	-12.22	-3.06	6.51	-15.26	-0.41
	F	2.440	-18.18	-10.70	7.50	-14.57	-0.41
	CH_3	2.413	-23.72	-15.71	8.29	-15.84	-0.46
	OH	2.417	-22.30	-14.78	8.20	-15.28	-0.44
	NH_2	2.402	-27.12	-19.28	8.52	-15.90	-0.46
Naph		**R_{min} (Å)**	**Total**	**Elec**	**Rep**	**Ind**	**Disp**
R1	H	2.428	-24.68	-13.84	7.40	-17.77	-0.46
	NO_2	2.506	-14.69	-2.43	5.46	-17.31	-0.41
	CN	2.495	-15.84	-3.56	5.63	-17.49	-0.43
	F	2.465	-20.84	-9.72	6.53	-17.22	-0.43
	CH_3	2.411	-25.64	-14.32	7.88	-18.69	-0.51
	OH	2.435	-24.20	-13.10	7.33	-17.95	-0.47
	NH_2	2.416	-28.41	-17.15	7.74	-18.50	-0.50
R2	H	2.428	-24.68	-13.84	7.40	-17.77	-0.46
	NO_2	2.476	-15.44	-3.31	6.19	-17.90	-0.43
	CN	2.467	-16.48	-4.45	6.39	-17.99	-0.44
	F	2.440	-22.04	-11.06	7.09	-17.62	-0.45
	CH_3	2.413	-26.30	-15.07	7.79	-18.53	-0.49
	OH	2.417	-25.89	-14.81	7.68	-18.27	-0.48
	NH_2	2.402	-28.96	-17.70	8.09	-18.86	-0.50

Table S5. Interaction energy decomposition at the minima of the complexes with sodium cation over the center of the rings of anthracene, obtained by interpolation from values along lines passing through ring centers. SAPT(DFT) values with PBE0/aug-cc-pVDZ.

		R_{min} (Å)	**Total**	**Elec**	**Rep**	**Ind**	**Disp**
R1	H	2.404	-26.47	-13.39	7.87	-20.44	-0.51
	NO_2	2.474	-17.40	-3.08	5.99	-19.86	-0.45
	CN	2.464	-18.39	-4.07	6.18	-20.04	-0.46
	F	2.440	-22.79	-9.47	7.00	-19.85	-0.47
	CH_3	2.390	-27.17	-13.72	8.32	-21.22	-0.55
	OH	2.414	-25.73	-12.46	7.75	-20.51	-0.51
	NH_2	2.398	-29.63	-16.22	8.11	-20.98	-0.53
R2	H	2.414	-26.21	-12.97	7.33	-20.04	-0.52
	NO_2	2.456	-17.67	-3.38	6.27	-20.08	-0.48
	CN	2.449	-18.71	-4.52	6.44	-20.14	-0.49
	F	2.425	-23.84	-10.51	7.07	-19.89	-0.51
	CH_3	2.402	-27.66	-14.10	7.65	-20.67	-0.54
	OH	2.405	-27.36	-13.93	7.59	-20.47	-0.54
	NH_2	2.393	-30.22	-16.63	7.93	-20.97	-0.55
R3	H	2.404	-26.47	-13.39	7.87	-20.44	-0.51
	NO_2	2.432	-18.93	-4.86	7.09	-20.69	-0.48
	CN	2.428	-19.90	-6.00	7.21	-20.62	-0.48
	F	2.410	-24.65	-11.49	7.71	-20.36	-0.50
	CH_3	2.395	-27.88	-14.54	8.11	-20.94	-0.52
	OH	2.395	-27.84	-14.58	8.12	-20.87	-0.52
	NH_2	2.386	-30.27	-16.82	8.39	-21.32	-0.53

Table S6. Nuclear Independent Chemical Shifts (NICS) obtained at the center of the rings and 1 Å above them for anthracene and derivatives (in ppm at the PBE0/aug-cc-pVDZ level). Δ_{NICS} is the change relative to unsubstituted anthracene. NICS(0) and NICS(1) correspond to NICS values on the ring centers and 1 Å above them.

		NICS(0)				NICS(1)	
	R1	**R2**	**R3**		**R1**	**R2**	**R3**
H	-7.09	-11.22	-7.01		-9.84	-13.35	-9.82
		$\Delta_{NICS(0)}$				$\Delta_{NICS(1)}$	
NO_2	-0.81	0.84	0.06		0.13	0.48	-0.03
CN	-0.24	0.37	-0.03		0.16	0.15	-0.11
F	-2.06	0.15	0.02		-0.21	0.15	0.01
CH_3	-0.33	0.21	0.13		-0.22	0.12	0.11
OH	-1.49	0.46	0.22		0.00	0.40	0.22
NH_2	-0.27	0.78	0.32		0.69	0.70	0.35

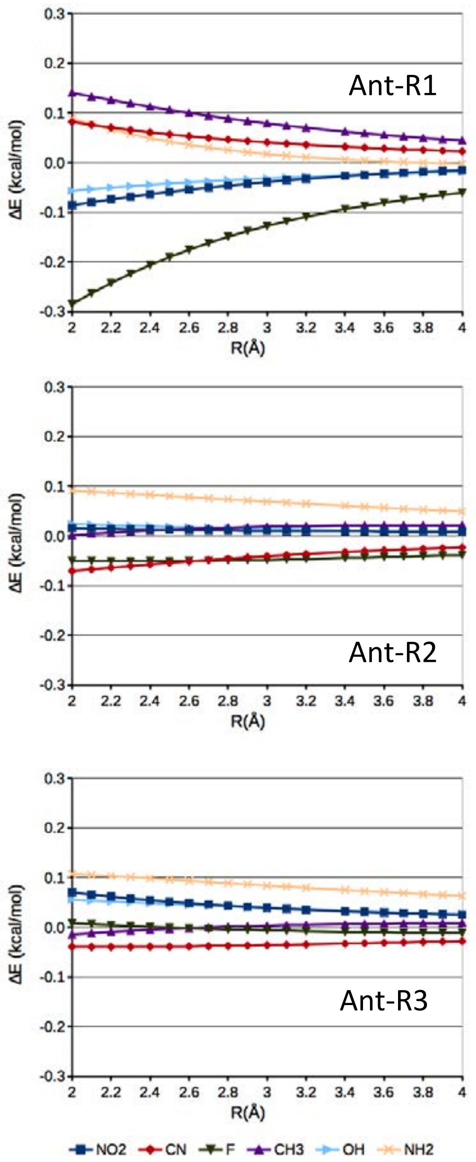


Figure S1. Differences on Molecular Electrostatic Potentials for substituted anthracenes along lines passing through ring centers employing fully and partially optimized geometries. The results correspond to MEP_{frozen} - MEP_{full}.

As described in the manuscript, the geometry of substituted anthracenes is kept frozen at the geometry of anthracene, and only the substituent group is relaxed. If the substituted anthracenes are fully optimized the geometry hardly changes, and the effects upon the results obtained for MEPs are marginal. As shown in Figure S1, the largest change for MEP on lines through ring centers hardly reaches 0.3 kcal mol^{-1} at most.

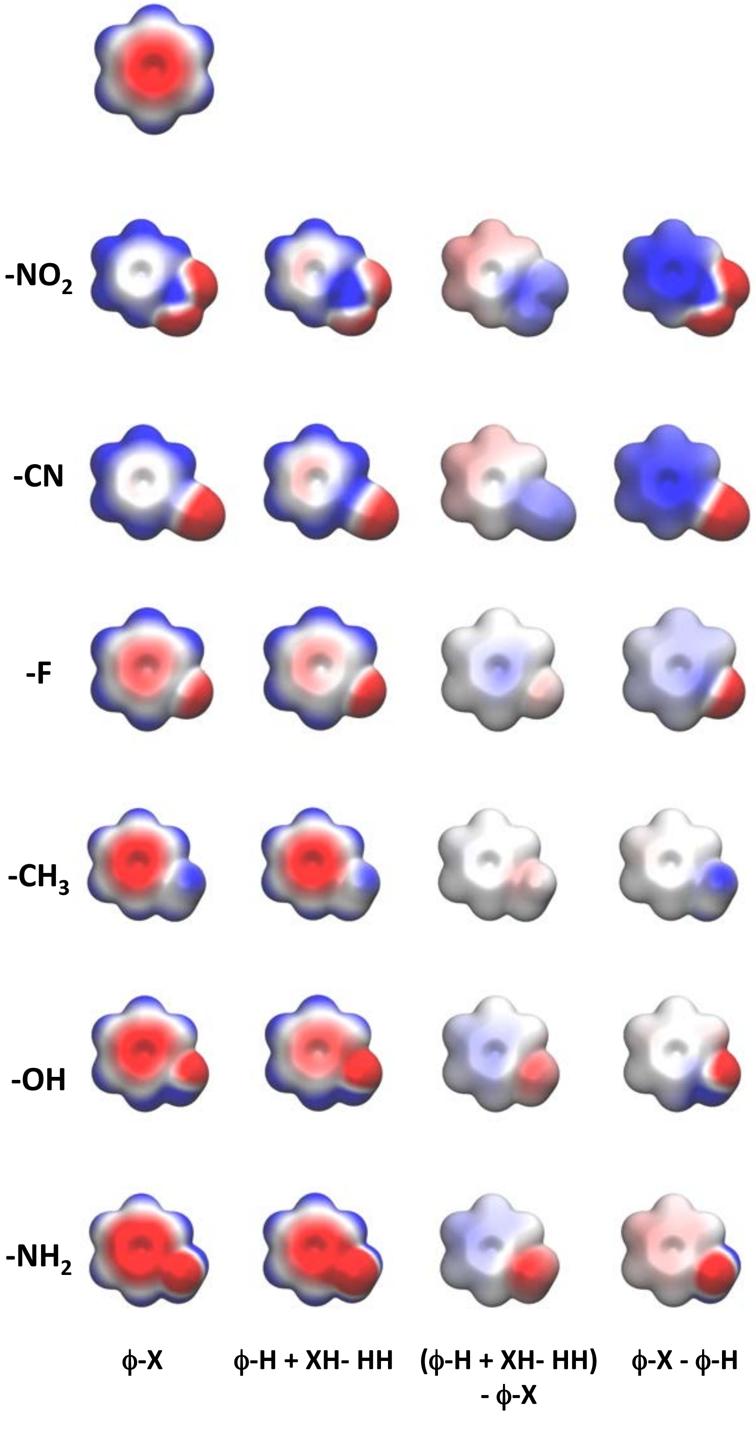


Figure S2. Molecular Electrostatic Potentials for substituted benzenes as mapped onto an isodensity surface of 0.002 a.u. Color scale runs from -15.0 kcal mol^{-1} (red) to 15.0 kcal mol^{-1} (blue), white corresponding to 0.0 kcal mol^{-1}.

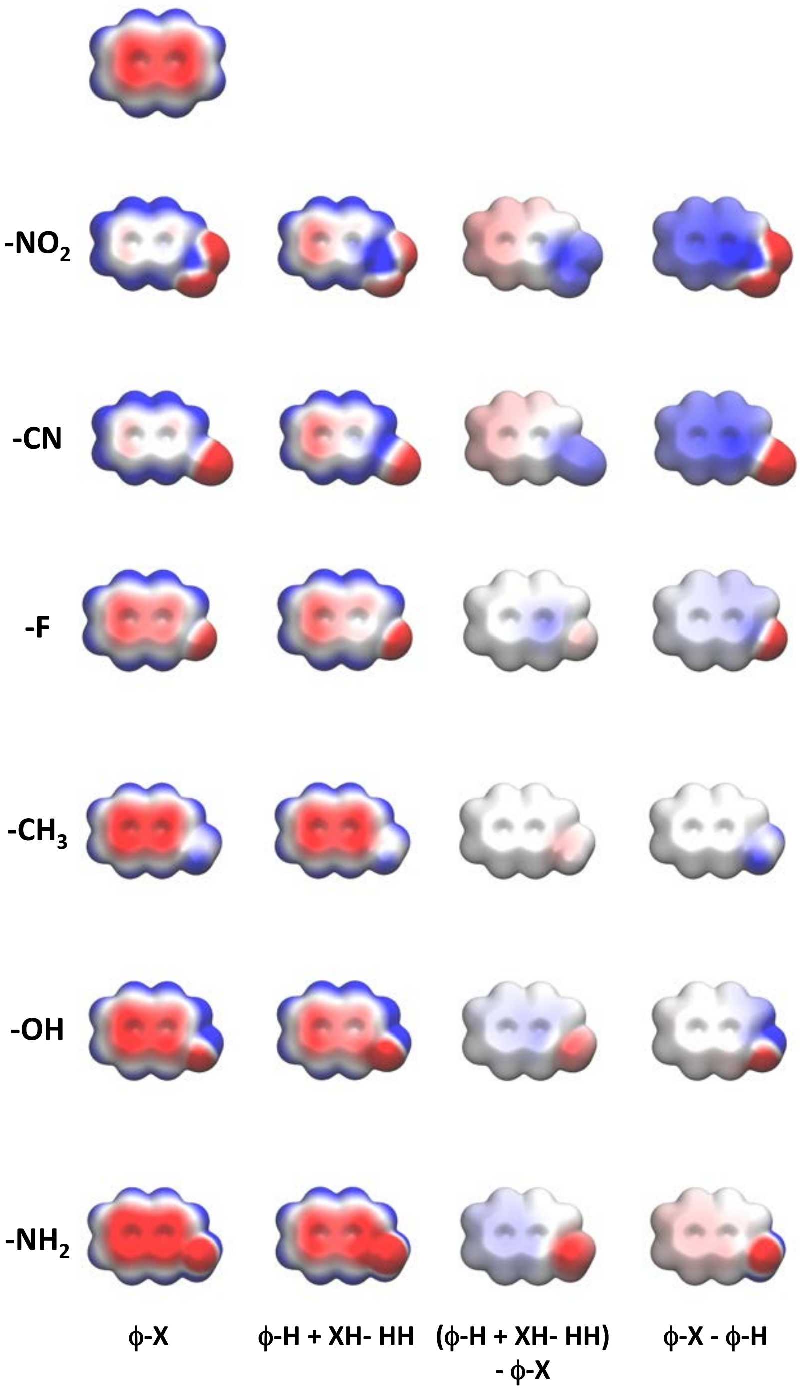


Figure S3. Molecular Electrostatic Potentials for substituted naphthalenes as mapped onto an isodensity surface of 0.002 a.u. Color scale runs from -15.0 kcal mol^{-1} (red) to 15.0 kcal mol^{-1} (blue), white corresponding to 0.0 kcal mol^{-1}.

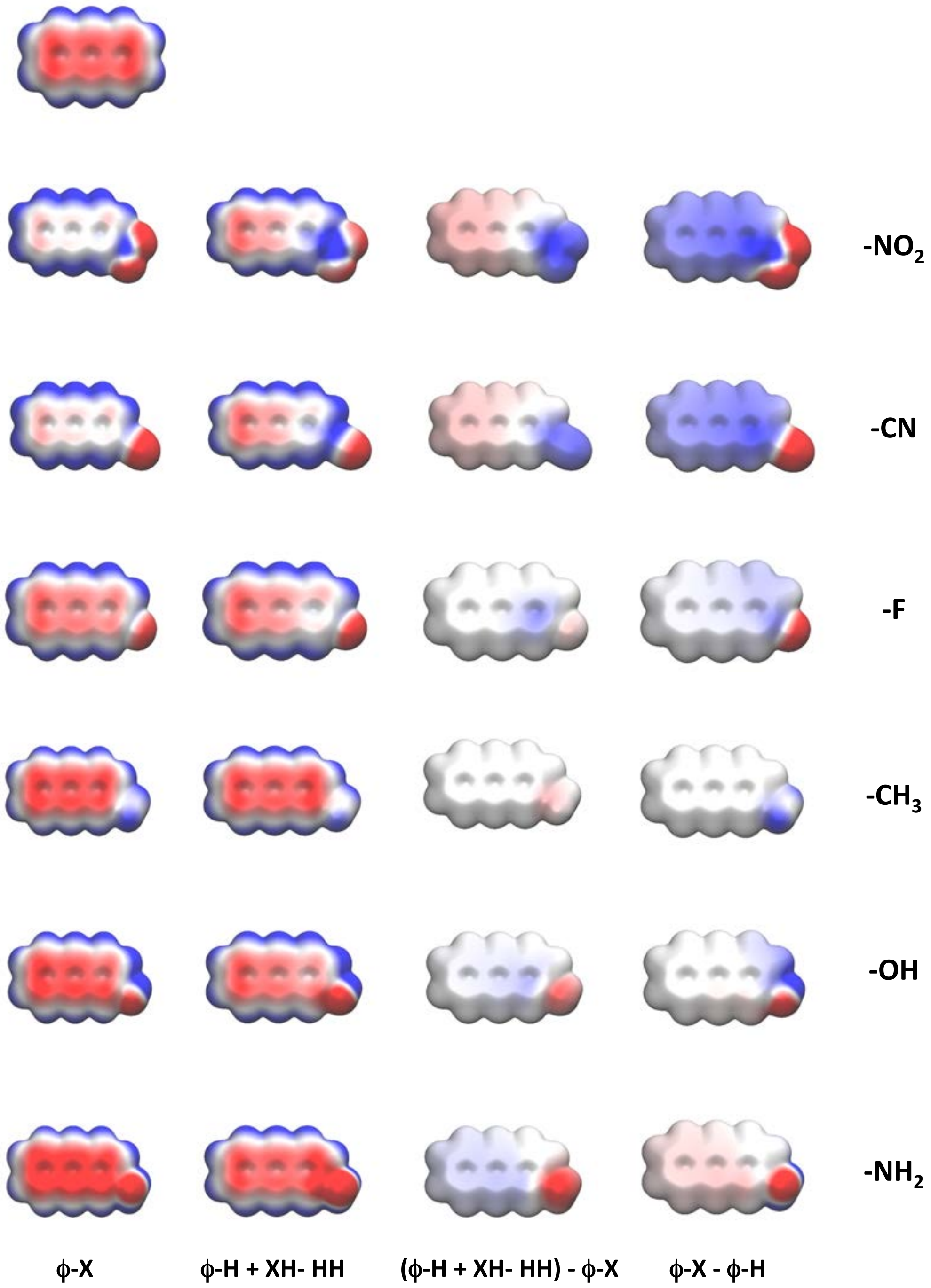


Figure S4. Molecular Electrostatic Potentials for substituted anthracenes as mapped onto an isodensity surface of 0.002 a.u. Color scale runs from -15.0 kcal mol^{-1} (red) to 15.0 kcal mol^{-1} (blue), white corresponding to 0.0 kcal mol^{-1}.

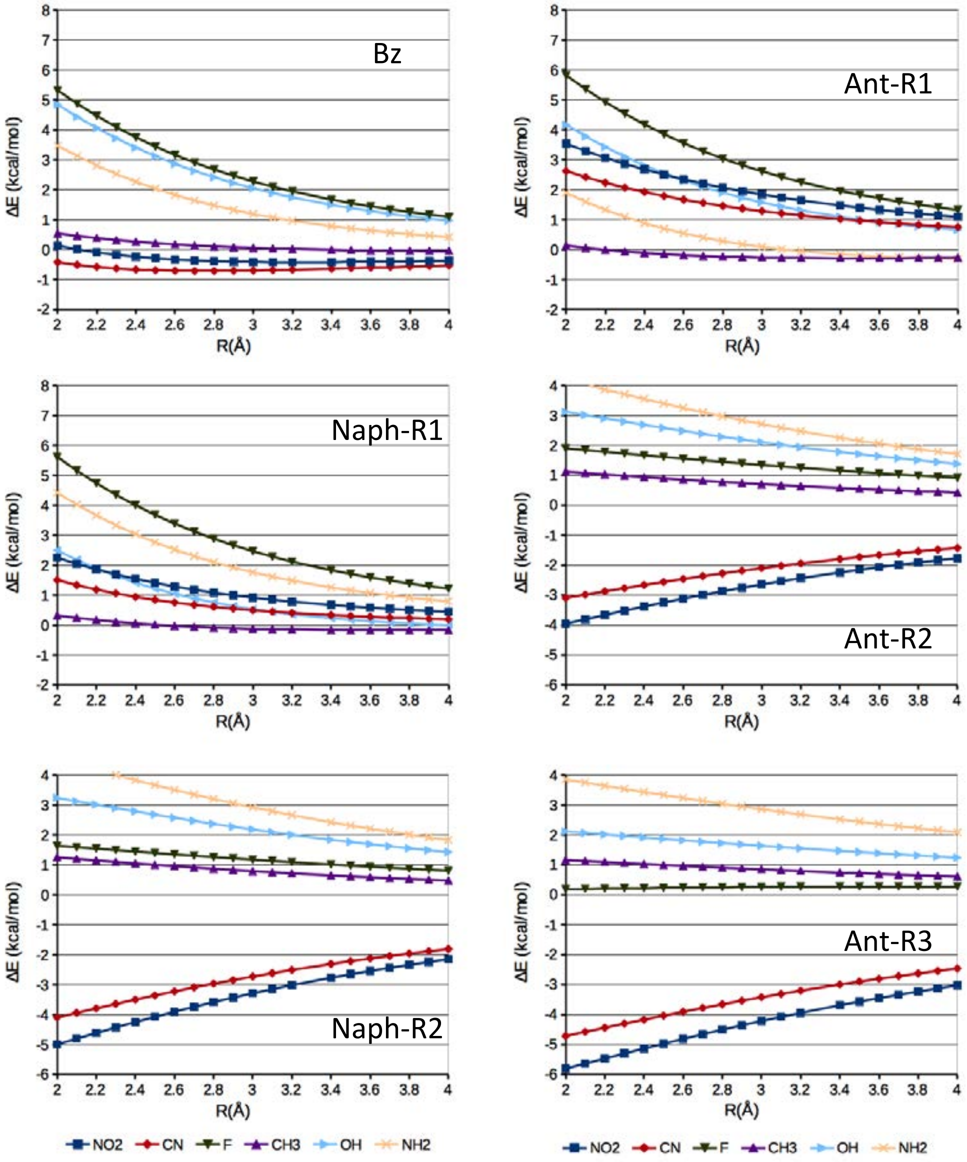


Figure S5. Deviations of the additive model relative to the computed MEPs on lines passing through the center of the rings. R1 is the ring nearest to the substituent.

The behavior is similar in the nearest ring for the three aromatic species, but deviations are already large in the second and third rings.

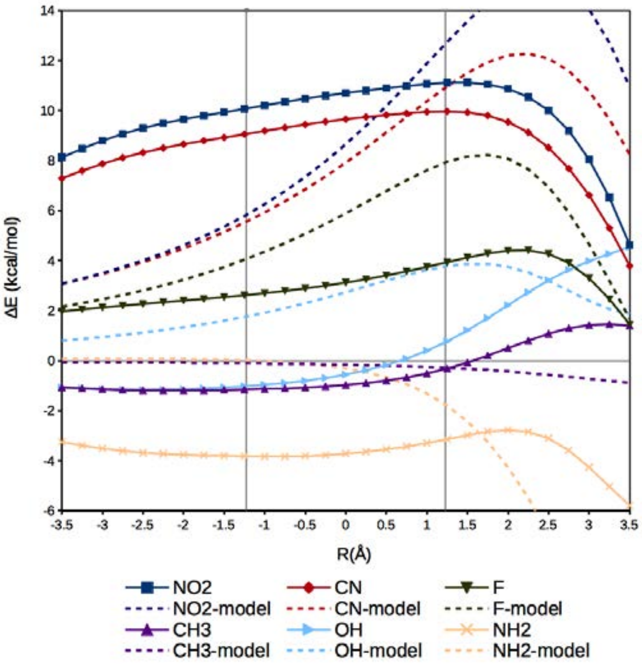


Figure S6. MEP changes upon substitution along a line 2.4 Å over the molecular plane of naphthalene derivatives. Vertical lines indicate the position of the ring centers. Solid lines correspond to the calculated changes on MEPs at the PBE/aug-cc-pVDZ level; dotted lines represent the values obtained from the additive model.

As for anthracene, the local model decays too quickly. MEP changes are much larger in the second ring than predicted by the model.

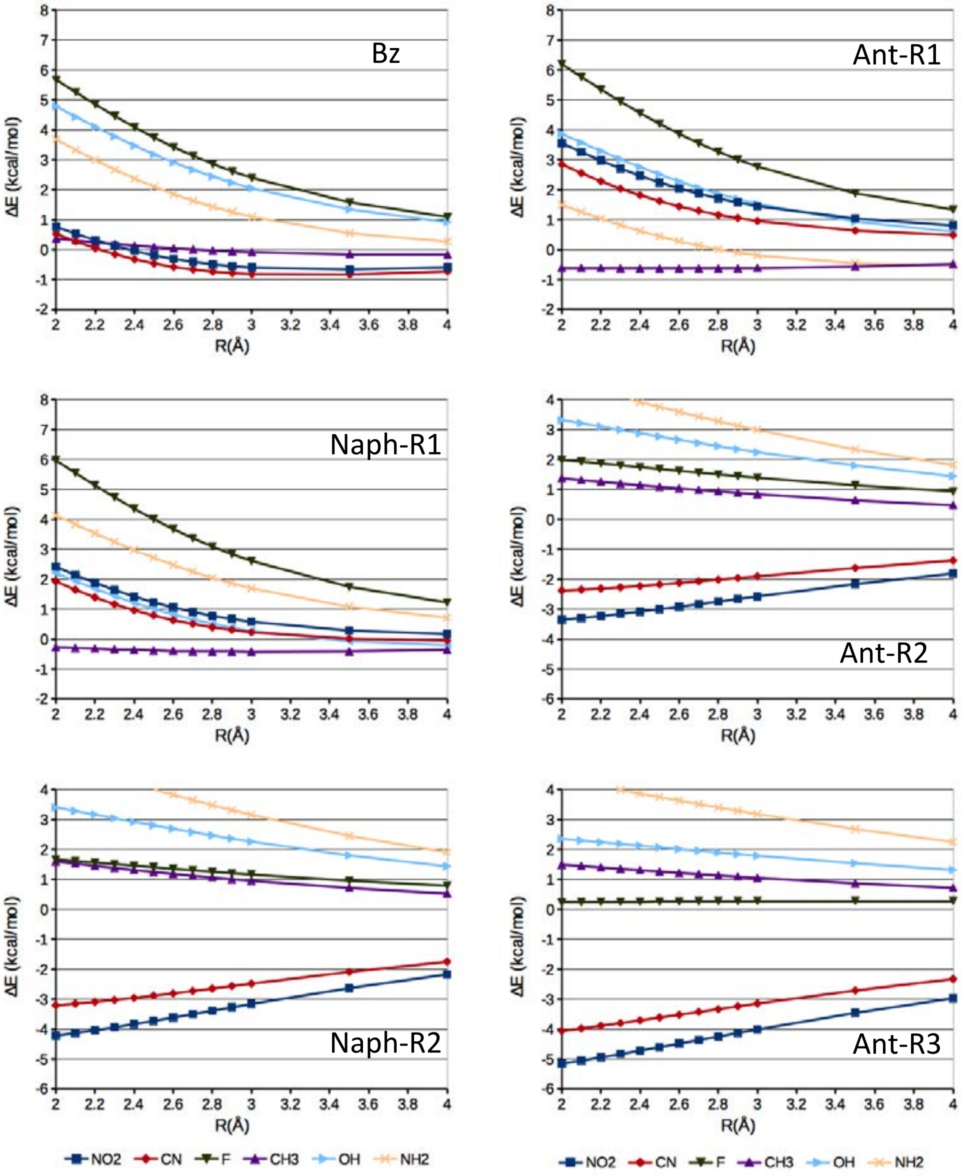


Figure S7. Deviations of the additive model relative to the computed SAPT(DFT) interaction energies on lines passing through the center of the rings.

The deviations in interaction energy mimic MEP deviations shown in Figure S4.

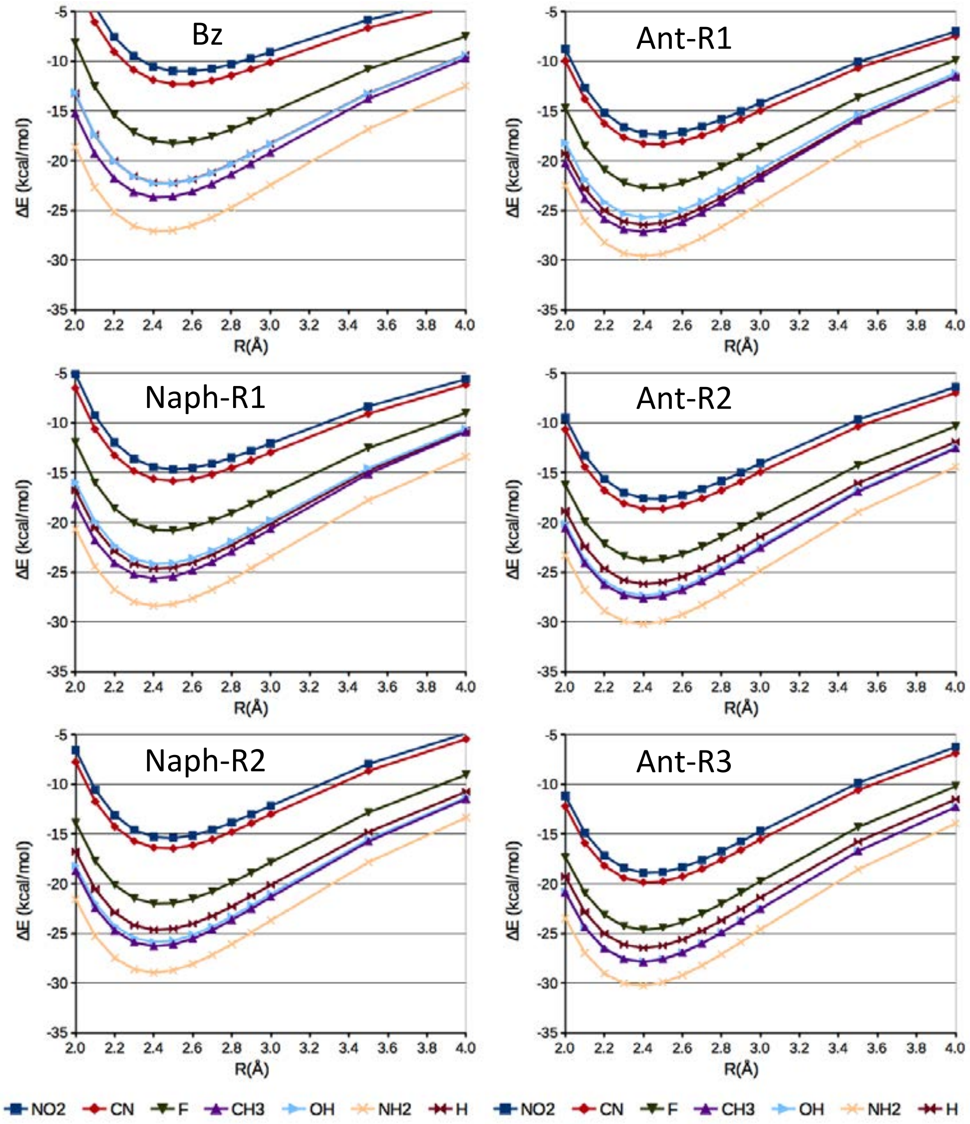
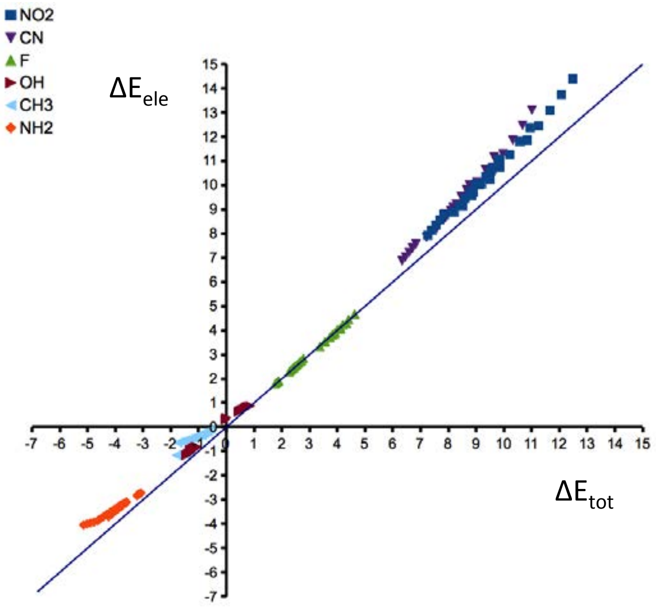


Figure S8. SAPT(DFT) interaction energies for Na$^+$ complexes. The cation is placed above the rings following a line passing through the ring centers.



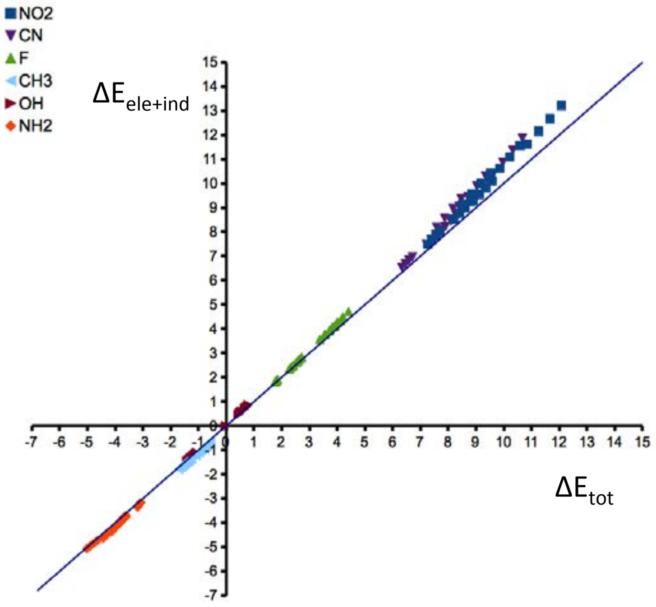


Figure S9. Correlation between total energy changes (kcal mol^{-1}) and: Top: electrostatic energy changes. Bottom: electrostatic + induction energy changes. Points between 2.2 and 2.6 Å above the ring centers of benzene, naphthalene and anthracene are employed. The blue line corresponds to x=y.

There is a pretty good correlation between electrostatic energy changes and total energy changes, which improves if induction is included. Therefore, monitoring electrostatic energy changes, total interaction energies could be predicted for cation···π complexes.

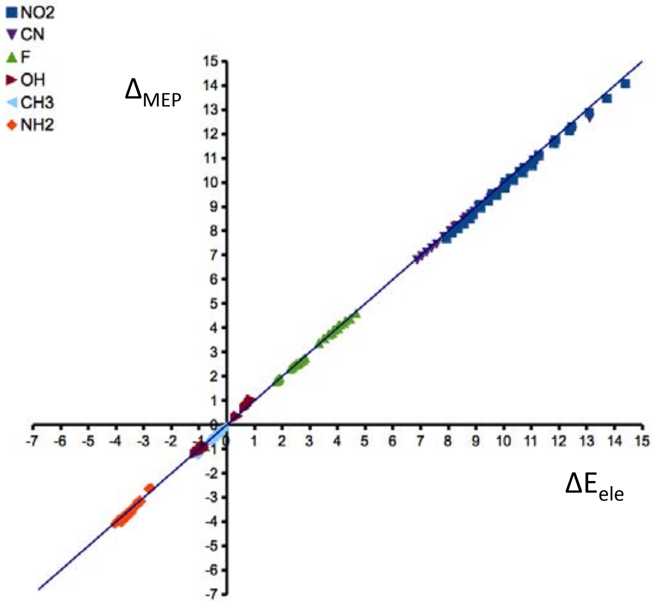


Figure S10. Correlation between electrostatic energy changes (kcal mol^{-1}) and MEP changes. Points between 2.2 and 2.6 Å above the ring centers of benzene, naphthalene and anthracene are employed. The blue line corresponds to x=y.

The correspondence between changes on MEP and changes in electrostatic energy is almost perfect in these cation···π complexes. Thus, MEP changes can be employed in order to assess changes in interaction energies due to substitution since as indicated in Fig. S8, the correspondence with total interaction energies is quite good. Thus, deviations observed with the through-space model are due to an inappropriate description of MEP changes because substituent effect reaches further than the model, as indicated in Figures 2 and S5.

CARTESIAN COORDINATES (Å) for UNSUBSTITUTED MOLECULES

Benzene

C	0.000000000000	0.000000000000	0.000000000000	
C	0.000000000000	0.000000000000	1.394994510000	
C	1.208100683800	0.000000000000	2.092491765000	
C	2.416201367600	0.000000000000	1.394994510000	
C	2.416201367600	0.000000000000	0.000000000000	
C	1.208100683800	0.000000000000	-0.697497255000	
H	-0.944750031494	0.000000000000	-0.545451685000	
H	-0.944750031494	0.000000000000	1.940446195000	
H	1.208100683800	0.000000000000	3.183395135000	
H	3.360951399094	0.000000000000	1.940446195000	
H	3.360951399094	0.000000000000	-0.545451685000	
H	1.208100683800	0.000000000000	-1.788400625000	x

Naphthalene

C	0.000000000000	0.000000000000	0.000000000000	
C	0.000000000000	0.000000000000	1.428853890000	
C	1.242046485882	0.000000000000	-0.686343762828	
C	-1.242046485882	0.000000000000	-0.686343762828	
C	-1.242046485882	0.000000000000	2.115197652828	
C	1.242046485882	0.000000000000	2.115197652828	
C	2.429708280708	0.000000000000	0.006836245380	
C	-2.429708280708	0.000000000000	0.006836245380	
C	-2.429708280708	0.000000000000	1.422017644620	
C	2.429708280708	0.000000000000	1.422017644620	
H	1.239458315647	0.000000000000	-1.777706743906	
H	-1.239458315647	0.000000000000	-1.777706743906	
H	-1.239458315647	0.000000000000	3.206560633906	
H	1.239458315647	0.000000000000	3.206560633906	
H	3.377629512454	0.000000000000	-0.532512128525	
H	-3.377629512454	0.000000000000	-0.532512128525	
H	-3.377629512454	0.000000000000	1.961366018525	
H	3.377629512454	0.000000000000	1.961366018525	x

Anthracene

C	0.000000000000	0.000000000000	0.000000000000	
C	0.000000000000	0.000000000000	1.439632560000	
C	1.221029706994	0.000000000000	-0.682472949967	
C	1.221029706994	0.000000000000	2.122105509967	
C	2.442059413988	0.000000000000	0.000000000000	
C	2.442059413988	0.000000000000	1.439632560000	
C	-1.252821337197	0.000000000000	-0.685663710809	
C	-1.252821337197	0.000000000000	2.125296270809	
C	3.694880751186	0.000000000000	-0.685663710809	
C	3.694880751186	0.000000000000	2.125296270809	
C	-2.432701360877	0.000000000000	0.007465853242	
C	-2.432701360877	0.000000000000	1.432166706758	
C	4.874760774865	0.000000000000	0.007465853242	
C	4.874760774865	0.000000000000	1.432166706758	
H	1.221029706994	0.000000000000	-1.774475949967	
H	1.221029706994	0.000000000000	3.214108509967	
H	-1.250509262092	0.000000000000	-1.777035371742	
H	-1.250509262092	0.000000000000	3.216667931742	
H	3.692568676080	0.000000000000	-1.777035371742	
H	3.692568676080	0.000000000000	3.216667931742	
H	-3.382903405861	0.000000000000	-0.528079774275	
H	-3.382903405861	0.000000000000	1.967712334275	
H	5.824962819850	0.000000000000	-0.528079774275	
H	5.824962819850	0.000000000000	1.967712334275	x

CARTESIAN COORDINATES (Å) for CAPPED SUBSTITUENTS

ben-no2.xyz

N	1.208100683800	0.000000000000	-2.159425625000
O	2.288816898332	0.000000000000	-2.722387844682
O	0.127384469267	0.000000000000	-2.722387844682
H	1.208100683800	0.000000000000	-1.117802495155

ben-cn.xyz

C	1.208100683800	0.000000000000	-2.131193645000
N	1.208100683800	0.000000000000	-3.292885095000
H	1.208100683800	0.000000000000	-1.055453622109

ben-f.xyz

F	1.208100683800	0.000000000000	-2.041874975000
H	1.208100683800	0.000000000000	-1.120337043575

ben-ch3.xyz

C	1.198018019327	0.000000000000	-2.203486153429
H	2.216193332348	0.000000000000	-2.611830199540
H	0.677296465108	0.884689849071	-2.597802244500
H	0.677296465108	-0.884689849071	-2.597802244500
H	1.205339893763	0.000000000000	-1.109860391455

ben-oh.xyz

O	1.147502839031	0.000000000000	-2.059487517955
H	2.041841248640	0.000000000000	-2.415438557207
H	1.190155370709	0.000000000000	-1.100834069851

ben-nh2.xyz

N	1.208086183869	0.061635599022	-2.092912823947
H	0.372311602256	-0.293050751459	-2.536454882728

```
 H         2.044094548841     -0.292702599256     -2.536536703949
 H         1.208096642125      0.017180155379     -1.086451960944
naf-no2.xyz
 N         3.696165211157      0.000000000000      2.147748727954
 O         3.653503011063      0.000000000000      3.366234572183
 O         4.720433110336      0.000000000000      1.486079094120
 H         2.792522388093      0.000000000000      1.629924813724
naf-cn.xyz
 C         3.674847514021      0.000000000000      2.131331681951
 N         4.684433141943      0.000000000000      2.706458734904
 H         2.740118141333      0.000000000000      1.598847725607
naf-f.xyz
 F         3.605746637357      0.000000000000      2.072572992121
 H         2.799362252659      0.000000000000      1.626501084142
naf-ch3.xyz
 C         3.739751377086      0.000000000000      2.166959145285
 H         4.593805427432      0.000000000000      1.478653006845
 H         3.831060630774      0.884758804708      2.813066038064
 H         3.831060630774     -0.884758804708      2.813066038064
 H         2.789113728947      0.000000000000      1.626389573069
naf-oh.xyz
 O         3.593817828257      0.000000000000      2.130506376876
 H         4.337070861759      0.000000000000      1.519847722635
 H         2.774145182765      0.000000000000      1.631645393653
naf-nh2.xyz
 N         3.655390872348      0.064124941017      2.085287868595
 H         4.437947443098     -0.329123979292      1.581258154460
 H         3.639684982940     -0.237013166669      3.049718134650
 H         2.770476231802      0.017828208472      1.606422022056
ant-no2.xyz
 N         6.141581173370      0.000000000000      2.155438996262
 O         7.164076100962      0.000000000000      1.490423000849
 O         6.103336411526      0.000000000000      3.374353858632
 H         5.237159313968      0.000000000000      1.639072769830
ant-cn.xyz
 C         6.121587450503      0.000000000000      2.137432260463
 N         7.133060128494      0.000000000000      2.709570194334
 H         5.185499132580      0.000000000000      1.607935371628
ant-f.xyz
 F         6.055986363702      0.000000000000      2.072620265621
 H         5.245861286733      0.000000000000      1.633375219283
ant-ch3.xyz
 C         6.189669995903      0.000000000000      2.170126455804
 H         7.039643023173      0.000000000000      1.476798706588
 H         6.283963713912     -0.885206648196      2.814976823237
 H         6.283963713912      0.885206648196      2.814976823237
 H         5.235968822443      0.000000000000      1.634885644364
ant-oh.xyz
 O         6.045860471555      0.000000000000      2.128412222417
 H         6.783277203920      0.000000000000      1.510907266303
 H         5.221093210887      0.000000000000      1.638069249774
ant-nh2.xyz
 N         6.106840849936      0.064763093305      2.079993927425
 H         6.101552347120     -0.214681276575      3.050977325004
 H         6.883433299938     -0.337307861487      1.573815433169
 H         5.216467745479      0.017961495253      1.611836098152
```

CARTESIAN COORDINATES (Å) for CAPPING H-H

```
ben-no2.xyz
 H         1.208100683800      0.000000000000     -1.117802495155
 H         1.208100683800      0.000000000000     -1.878869673337
ben-cn.xyz
 H         1.208100683800      0.000000000000     -1.055453622109
 H         1.208100683800      0.000000000000     -1.816677911614
ben-f.xyz
 H         1.208100683800      0.000000000000     -1.120337043575
 H         1.208100683800      0.000000000000     -1.881401221882
ben-ch3.xyz
 H         1.205339893763      0.000000000000     -1.109860391455
 H         1.200244556941      0.000000000000     -1.870921191268
ben-oh.xyz
 H         1.190155370709      0.000000000000     -1.100834069851
 H         1.156326238022      0.000000000000     -1.861173806341
ben-nh2.xyz
 H         1.208096642125      0.017180155379     -1.086451960944
 H         1.208088740918      0.050766220238     -1.846832626462
naf-no2.xyz
 H         2.792522388093      0.000000000000      1.629924813724
 H         3.452857082477      0.000000000000      2.008323321874
naf-cn.xyz
 H         2.740118141333      0.000000000000      1.598847725607
 H         3.401550014634      0.000000000000      1.975643267759
naf-f.xyz
 H         2.799362252659      0.000000000000      1.626501084142
 H         3.465324292312      0.000000000000      1.994894822051
```

```
naf-ch3.xyz
 H         2.789113725718      0.000000000000      1.626389571233
 H         3.450706557971      0.000000000000      2.002597009485
naf-oh.xyz
 H         2.774145182765      0.000000000000      1.631645393653
 H         3.424294337828      0.000000000000      2.027332682377
naf-nh2.xyz
 H         2.770476231802      0.017828208472      1.606422022056
 H         3.439166988816      0.052812596473      1.968279709520
ant-no2.xyz
 H         5.237159313968      0.000000000000      1.639072769830
 H         5.898094412441      0.000000000000      2.016423846838
ant-cn.xyz
 H         5.185499132580      0.000000000000      1.607935371628
 H         5.848073835584      0.000000000000      1.982719713173
ant-f.xyz
 H         5.245861286733      0.000000000000      1.633375219283
 H         5.914911777841      0.000000000000      1.996130455881
ant-ch3.xyz
 H         5.235968822443      0.000000000000      1.634885644364
 H         5.899664667382      0.000000000000      2.007368254725
ant-oh.xyz
 H         5.221093210887      0.000000000000      1.638069249774
 H         5.875300929816      0.000000000000      2.027010679585
ant-nh2.xyz
 H         5.216467745479      0.017961495253      1.611836098152
 H         5.889420122630      0.053334583800      1.965674194243
```