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Supplementary Material for

Anion-π Interactions and Positive Electrostatic Potentials of *N*-Heterocycles Arise from the Positions of the Nuclei, not Changes in the π-electron Distribution

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Contents

Computing the σ- and π-contributions to the electronic component of the ESP and Q_{zz}

The electrostatic potential of a collection of nuclei and the associated electron density is given by

$$V(\mathbf{r}) = V^{nuc}(\mathbf{r}) + V^{elec}(\mathbf{r}) = \sum_{A}^{nuclei} \frac{Z_A}{|\mathbf{r} - \mathbf{R_A}|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{1}$$

where the integral runs over all space. We wish to partition $\rho(\mathbf{r})$ into contributions from the σ- and π-sytems, such that

$$V(\mathbf{r}) = V_{\sigma}^{nuc}(\mathbf{r}) + V_{\sigma}^{elec}(\mathbf{r}) + V_{\pi}^{elec}(\mathbf{r}). \tag{2}$$

For planar arenes, this can be accomplished by partitioning the electron density based on the symmetry of the underlying molecular orbitals. For a C_s-symmetric arene in which the mirror-plane corresponds to the molecular plane, the contributions of the σ- and π-electrons to the electrostatic potential can be defined as

$$V_{a'}^{elec}(\mathbf{r}) = -\int \frac{\rho_{a'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \equiv V_{\sigma}^{elec}(\mathbf{r}) \tag{3}$$

and

$$V_{a''}^{elec}(\mathbf{r}) = -\int \frac{\rho_{a''}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \equiv V_{\pi}^{elec}(\mathbf{r}), \tag{4}$$

where

$$\rho_{a'}(\mathbf{r}) = 2\sum_{i}^{a'} \left|\phi_i^s(\mathbf{r})\right|^2 \tag{5}$$

and

$$\rho_{a''}(\mathbf{r}) = 2\sum_{i}^{a''} \left|\phi_i^s(\mathbf{r})\right|^2 \tag{6}$$

in which the sums run over all doubly-occupied molecular orbitals of a' or a'' symmetry.

The σ- and π-components of Q_{zz} are defined similarly.

Table S1. CCSD(T) interaction energies [$E_{CCSD(T)}$, from Ref. 5d in the main text] for Cl^- interacting with benzene and five azines at the corresponding equilibrium distances (in Angstroms), along with computed Q_{zz} values (in Buckinghams) and ESP values at the position of the anion and the Pearson correlation coefficient between the CCSD(T) interaction energies and the Qzz and ESP values.[a]

	R	$E_{CCSD(T)}$	Q_{zz}	ESP@R
benzene	3.88	0.9	–8.9	–6.6
pyridine	3.59	–1.3	–5.9	–4.9
pyrazine	3.39	–4.0	–2.9	–2.1
s-triazine	3.26	–7.0	0.3	1.8
s-tetrazine	3.17	–9.7	2.5	4.7
hexazine	3.04	–15.1	7.0	11.9
		Correlation:	–0.995	–0.997

[a] All energies in kcal mol^{-1}.

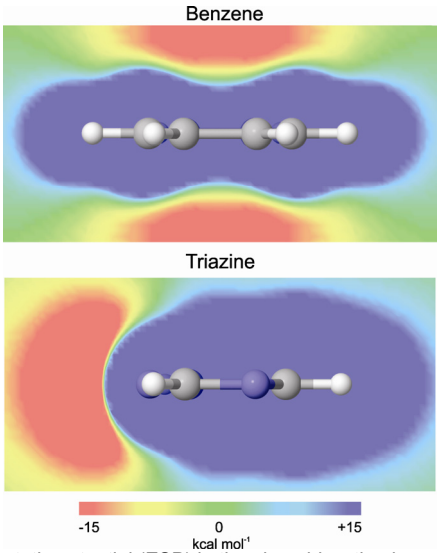

Figure S1. Electrostatic potential (ESP) in the plane bisecting benzene and triazine.

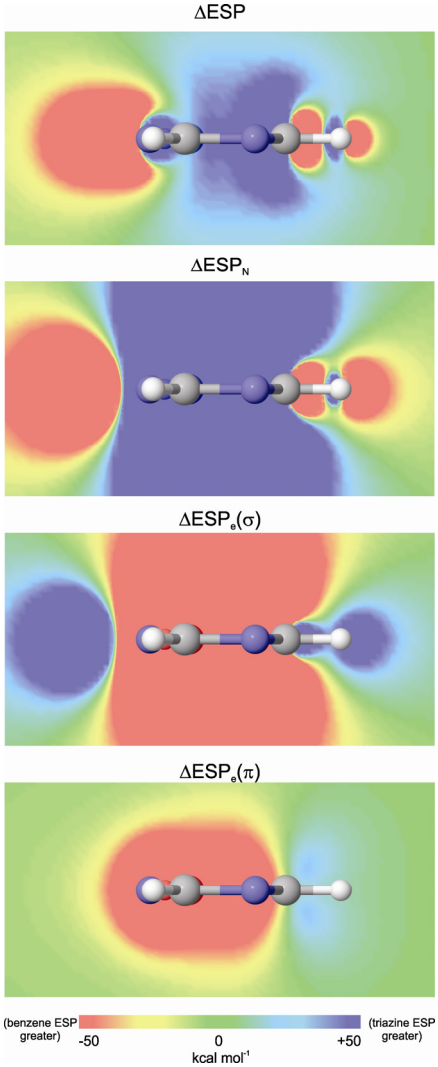

Figure S2. Difference in electrostatic potential (ΔESP) between triazine and benzene in the plane bisecting the two rings, along with the nuclear contribution to ΔESP (ΔESP$_N$) and hte s- and p-contributions to the electronic component of ΔESP$_N$, ΔESP$_e$(σ) and ΔESP$_e$(π).

MP2/aug-cc-pVTZ optimized Cartesian Coordinates

12
Benzene

C	-1.2074430	0.6971180	0.0000000
C	0.0000000	1.3942360	0.0000000
C	-1.2074430	-0.6971180	0.0000000
C	1.2074430	-0.6971180	0.0000000
C	0.0000000	-1.3942360	0.0000000
C	1.2074430	0.6971180	0.0000000
H	-2.1446600	1.2382200	0.0000000
H	-0.0000000	2.4764410	0.0000000
H	2.1446600	1.2382200	0.0000000
H	2.1446600	-1.2382200	0.0000000
H	0.0000000	-2.4764410	0.0000000
H	-2.1446600	-1.2382200	0.0000000

11
Pyridine

N	-1.399004	0.000000	0.000000
C	-0.698037	1.142655	0.000000
C	-0.698037	-1.142655	0.000000
C	1.407180	0.000000	0.000000
C	0.693948	-1.194555	0.000000
C	0.693948	1.194555	0.000000
H	-1.280633	2.056305	0.000000
H	1.200592	2.149983	0.000000
H	2.489086	0.000000	0.000000
H	1.200592	-2.149983	0.000000
H	-1.280633	-2.056305	0.000000

10
Pyrazine

N	-1.411837	0.000000	0.000000
C	-0.696633	1.132099	0.000000
C	-0.696633	-1.132099	0.000000
N	1.411837	0.000000	-0.000000
C	0.696633	-1.132099	-0.000000
C	0.696633	1.132099	-0.000000
H	-1.250488	2.062752	0.000000
H	1.250488	2.062752	-0.000000
H	1.250488	-2.062752	-0.000000
H	-1.250488	-2.062752	0.000000

9
s-Triazine

N	1.1897460	0.6869000	0.0000000
C	0.0000000	1.2942960	0.0000000
C	1.1208940	-0.6471480	0.0000000
C	-1.1208940	-0.6471480	0.0000000
N	0.0000000	-1.3738000	0.0000000
N	-1.1897460	0.6869000	0.0000000
H	0.0000000	2.3768120	0.0000000
H	-2.0583800	-1.1884060	0.0000000
H	2.0583800	-1.1884060	0.0000000

8
s-Tetrazine

C	-1.263225	0.000000	0.000000
C	1.263225	0.000000	-0.000000
H	-2.344128	0.000000	0.000000
H	2.344128	0.000000	-0.000000
N	-0.665524	1.198400	0.000000
N	0.665524	1.198400	-0.000000
N	-0.665524	-1.198400	0.000000
N	0.665524	-1.198400	-0.000000