Electronic Supplementary Information

Unveiling the Regioselectivity in Electrophilic Aromatic Substitution Reactions of Deactivated Benzenes through Molecular Electron Density Theory

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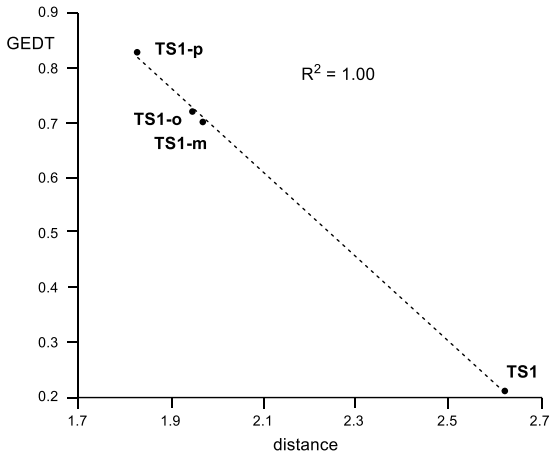

Figure S1. Plot of the GEDT, in average number of electrons, e, vs the distance. In Angstroms, between nitronium NO_2^+ ion **4** and the aromatic ring at the TSs involved in the nitration of benzene **1** and benzenesulfonic acid **8**.

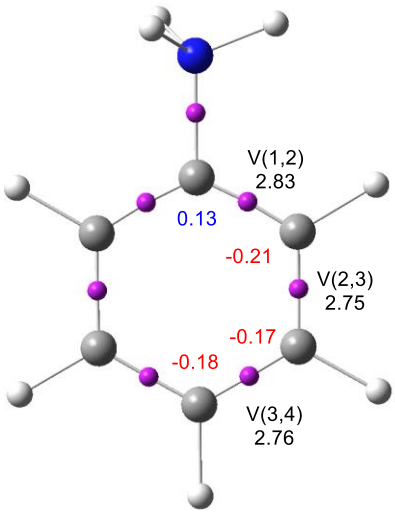

Figure S2. *ω*B97X-D/6-311G(d,p) ELF basin attractor positions, together with the valence basin populations of protonated aniline. Negative charges are coloured in red and positive charges in blue. ELF valence basin populations and natural atomic charges are given in average number of electrons, e.

Table S1. *ω*B97X-D/6-311G(d,p) electronic chemical potential, μ, chemical hardness, η, electrophilicity, ω, and nucleophilicity, *N*, in eV, of benzene **1**, benzenesulfonic acid **8**, and nitronium NO_2^+ ion **4**.

	μ	η	ω	*N*
nitronium NO_2^+ ion **4**	-16.05	14.11	9.12	-11.71
benzenesulfonic acid **8**	-4.78	10.18	1.12	1.53
benzene **1**	-3.66	10.71	0.62	2.38

Table S2. ωB97X-D/6-311G(d,p) electronic energies (E, in a.u.), enthalpies (H, in a.u.), entropies (S, in cal/mol.K) and Gibbs free energies (G, in a.u.), computed at 25 ºC, 1 atm and ε = 20.0, for the stationary points involved in the EAS nitration reaction of benzene **1** with nitronium NO_2^+ ion **4**.

	E	H	S	G
1	-232.221871	-232.115478	68.91	-232.148220
4	-204.816054	-204.800201	50.97	-204.824418
H_2SO_4	-700.230264	-700.184899	72.06	-700.219138
HSO_4^-	-699.795161	-699.763184	68.97	-699.795952
MC	-437.043726	-436.920092	91.86	-436.963740
TS	-437.041944	-436.920104	89.10	-436.962479
IN	-437.063157	-436.940566	85.84	-436.981353
3	-436.716048	-436.604334	84.01	-436.644250

Table S3. ωB97X-D/6-311G(d,p) electronic energies (E, in a.u.), enthalpies (H, in a.u.), entropies (S, in cal/mol.K) and Gibbs free energies (G, in a.u.), computed at 25 ºC, 1 atm and ε = 20.0, for the stationary points involved in the EAS nitration reaction of benzenesulfonic acid **8** with nitronium NO_2^+ ion **4**.

	E	H	S	G
8	-856.030728	-855.905070	92.72	-855.949126
4	-204.816054	-204.800201	50.97	-204.824418
CM-m	-1060.848966	-1060.705960	120.49	-1060.763207
TS-o	-1060.837645	-1060.696748	106.75	-1060.747467
TS-m	-1060.838303	-1060.697491	107.54	-1060.748587
TS-p	-1060.833897	-1060.693126	107.81	-1060.744347
IN-o	-1060.840672	-1060.698858	107.56	-1060.749962
IN-m	-1060.849280	-1060.707488	109.50	-1060.759517
IN-p	-1060.845238	-1060.704057	106.83	-1060.754814
9	-1060.513122	-1060.382015	102.16	-1060.430556
10	-1060.518656	-1060.387861	107.30	-1060.438844
11	-1060.518301	-1060.387610	107.77	-1060.438815

Table S4. ωB97X-D/6-311G(d,p) total and relative electronic energies (E, in a.u., ΔE in kcal/mol), enthalpies (H, in a.u. ΔH in kcal/mol), entropies (S, in cal/mol.K, ΔS, in cal/mol.K) and Gibbs free energies (G, in a.u., ΔG in kcal/mol), computed at 25 ºC, 1 atm and ε = 40.0, for the **TS-0**, **TS-m** and **TS-p**.

	E	ΔE	H	ΔH	S	ΔS	G	ΔG
8	-856.031329		-855.905668		92.61		-855.949668	
4	-204.818956		-204.803121		50.98		-204.827344	
TS-o	-1060.840207	6.32	-1060.699378	5.91	107.24	-36.35	-1060.750333	16.74
TS-m	-1060.841023	5.81	-1060.700274	5.34	107.96	-35.63	-1060.751570	15.97
TS-p	-1060.836610	8.58	-1060.695825	8.14	107.95	-35.64	-1060.747116	18.76

Table S5. ELF valence basin populations, distances of the N7-C5 forming bond, relative[a] electronic energies, GEDT and IRC values of the structures of the IRC associated to electrophilic attack of nitronium NO_2^+ ion **4** on benzenesulfonic acid **8**, defining the eights phases of the BET. Distances are given in angstroms, Å, GEDT values and electron populations in average number of electrons, e, relative energies in kcal·mol^{-1}.

tures	**S1**	**S2**	**S3**	**S4**	**TS-m**	**S5**	**S6**	**S7**	**S8**	**S9**
Phases	*I*	*II*	*III*	*IV*		*V*	*VI*	*VII*	*VIII*	
DE	0.0	2.4	3.4	6.7	6.8	6.8	5.6	5.6	0.1	-0.4
GEDT	0	-0.03	-0.07	-0.57	-0.77	-0.79	-1.03	-1.03	-1.11	-1.10
d(N7-C5)	3.166	2.689	2.594	2.081	1.888	1.874	1.622	1.620	1.530	1.533
V(C1,C2)	2.80	2.82	2.84	2.97	3.03	3.03	3.09	3.09	3.08	3.08
V(C2,C3)	2.77	2.75	2.73	2.46	2.31	2.30	2.13	2.13	2.13	2.13
V(C3,C4)	2.72	2.72	2.70	2.46	2.32	2.30	2.14	2.14	2.13	2.14
V(C4,C5)	2.74	2.74	2.75	2.82	2.86	2.86	2.90	2.90	2.88	2.88
V(C5,C6)	2.74	2.72	2.71	2.60	2.55	2.55	2.49	2.50	2.52	2.52
V(C1,C6)	2.85	2.82	2.80	2.63	2.56	2.55	2.47	2.47	2.49	2.50
V(N7,O8)	2.92	2.97	2.82	2.02	1.97	1.94	1.91	1.89	2.16	2.09
V(O8)	4.90	3.91	3.93	2.36	2.57	2.58	2.73	2.73	2.80	2.80
V'(O8)		0.99	1.00	2.91	2.82	2.82	2.82	2.81	2.76	2.76
V(N7)			0.25	1.73	1.87		0.06	0.23	0.10	0.20
V'(N7)								0.23		
V(C5)				0.09	0.22					
V(C5,N7)						2.12	2.24	1.94	2.12	2.10