How Amino and Nitro Substituents Direct Electrophilic Aromatic Substitution in Benzene: Explanation with Kohn-Sham Molecular Orbital Theory and Voronoi Deformation Density Analysis

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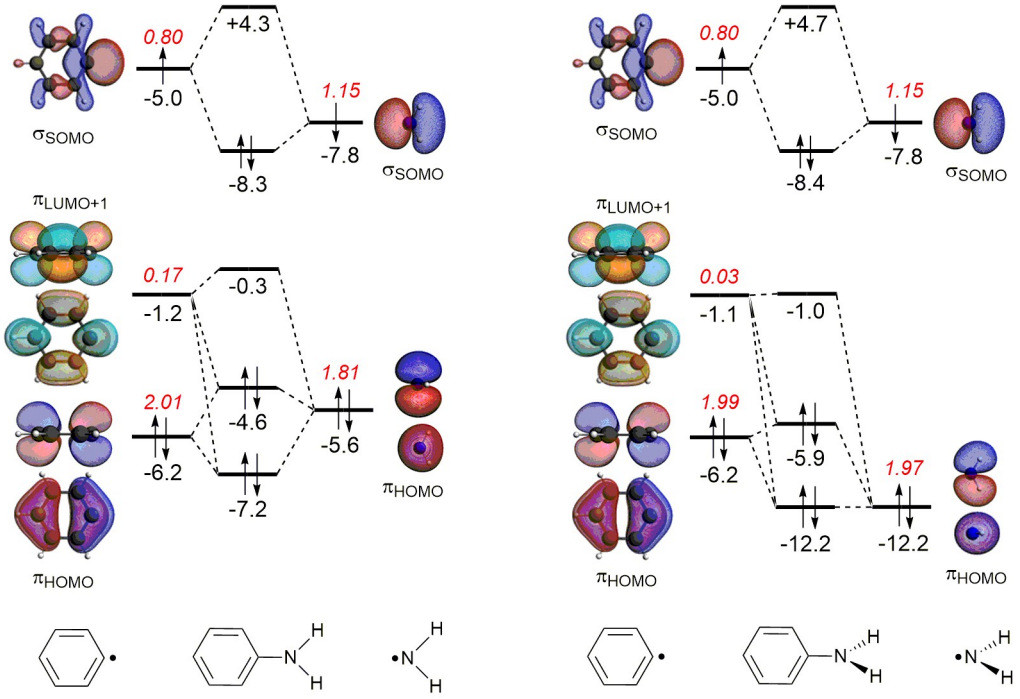
Electronic Supplementary Information



a) **b)**

Figure S3. MO diagrams for combination of two fragments into aniline in coplanar (a) and perpendicular (b) orientations (black numbers denotes MO energy in eV, red – gross electron population).

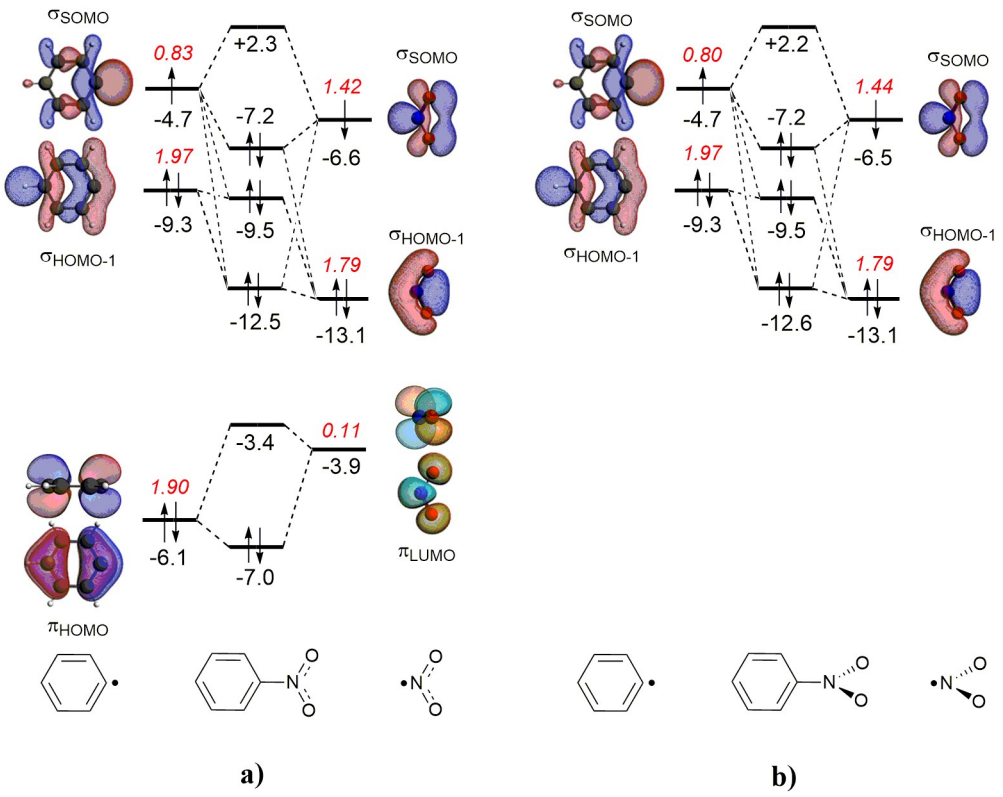


Figure S4. MO diagrams for combination of two fragments into the nitrobenzene in coplanar (a) and perpendicular (b) orientations (black numbers denotes MO energy in eV, red – gross electron population).

Table S1. Interaction energy and energy barrier for substituent rotation in substituted benzenes (in kcal/mol).

System	Angle	ΔE_{int}	ΔE_{rel}
Ph· ·NO_2	0	-74.1	0.0
Ph· ·NO_2	90	-68.8	5.1
Ph· ·NH_2	0	-143.6	0.0
Ph· ·NH_2	90	-133.7	9.0
NH_2Ph· ·NO_2	0	-80.4	0.0
NH_2Ph· ·NO_2	90*	-76.1	12.7
NH_2Ph· ·NO_2	90	-71.9	8.2
NO_2Ph· ·NH_2	0	-148.9	0.0
NO_2Ph· ·NH_2	90	-146.0	8.2
NO_2Ph· ·NH_2	90*	-134.8	12.7

* the NH_2 group is rotated

Table S2. Cartesian coordinates of aniline and nitrobenzene at the BLYP/TZ2P level of theory

Aniline				Nitrobenzene			
C	0.000000	-0.938168	0.000000	C	-0.000228	-0.231661	0.000000
C	-1.212904	-0.215413	0.000000	C	-1.223148	0.445411	0.000000
C	-1.206054	1.181191	0.000000	C	-1.214612	1.842623	0.000000
C	0.000000	1.894712	0.000000	C	0.000647	2.539940	0.000000
C	1.206054	1.181191	0.000000	C	1.215447	1.841824	0.000000
C	1.212904	-0.215413	0.000000	C	1.223115	0.444596	0.000000
H	-2.159126	-0.756101	0.000000	H	-2.147993	-0.121093	0.000000
H	-2.154155	1.715260	0.000000	H	-2.156170	2.386006	0.000000
H	0.000000	2.981594	0.000000	H	0.000992	3.627575	0.000000
H	2.154155	1.715260	0.000000	H	2.157358	2.384595	0.000000
H	2.159126	-0.756101	0.000000	H	2.147580	-0.122521	0.000000
N	0.000000	-2.327115	0.000000	N	-0.000836	-1.724045	0.000000
H	-0.863378	-2.846998	0.000000	O	-1.101947	-2.302169	0.000000
H	0.863378	-2.846998	0.000000	O	1.099794	-2.303079	0.000000