Is Aromatic Nitration Spin Density Driven?

– Supplementary Materials –

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- CM5 (ωB97X-D/ma-TZVP) net atomic charge of NO_2 as a function of the distance between interacting units for all the energy profiles (Figures S1-S4).
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Cartesian coordinates (Å) at *r* = 3.05 Å.

$^1A_{1g}$ benzene:NO_2^+, path A, gas phase

C	0.000000	1.387377	0.000000
C	1.201504	0.693689	0.000000
C	1.201504	-0.693689	0.000000
C	0.000000	-1.387377	0.000000
C	-1.201504	-0.693689	0.000000
C	-1.201504	0.693689	0.000000
H	-0.000000	2.470242	0.000000
H	2.139292	1.235121	0.000000
H	2.139292	-1.235121	0.000000
H	0.000000	-2.470242	0.000000
H	-2.139292	-1.235121	0.000000
H	-2.139292	1.235121	0.000000
N	0.000000	0.000000	3.050000
O	1.109086	0.000000	3.050000
O	-1.109086	0.000000	3.050000

$^1A_{1g}$ benzene:NO_2^+, path B, gas phase

C	0.000000	0.693689	0.000000
C	1.201504	0.000000	0.000000
C	1.201504	-1.387377	0.000000
C	0.000000	-2.081066	0.000000
C	-1.201504	-1.387377	0.000000
C	-1.201504	0.000000	0.000000
H	-0.000000	1.776553	0.000000
H	2.139292	0.541432	0.000000
H	2.139292	-1.928810	0.000000
H	0.000000	-3.163931	0.000000
H	-2.139292	-1.928810	0.000000
H	-2.139292	0.541432	0.000000
N	0.000000	0.000000	3.050000
O	1.109086	0.000000	3.050000
O	-1.109086	0.000000	3.050000

$^1A_{1g}$ benzene:NO_2^+, path C, gas phase

C	-1.201504	1.387377	0.000000
C	0.000000	0.693689	0.000000
C	0.000000	-0.693689	0.000000
C	-1.201504	-1.387377	0.000000
C	-2.403008	-0.693689	0.000000
C	-2.403008	0.693689	0.000000
H	-1.201504	2.470242	0.000000
H	0.937788	1.235121	0.000000
H	0.937788	-1.235121	0.000000
H	-1.201504	-2.470242	0.000000
H	-3.340797	-1.235121	0.000000
H	-3.340797	1.235121	0.000000
N	0.000000	0.000000	3.050000
O	1.109086	0.000000	3.050000
O	-1.109086	0.000000	3.050000

$^1A_{1g}$ benzene:NO_2^+, path D, gas phase

C	0.000000	0.000000	0.000000
C	1.201504	-0.693689	0.000000
C	1.201504	-2.081066	0.000000
C	0.000000	-2.774755	0.000000
C	-1.201504	-2.081066	0.000000
C	-1.201504	-0.693689	0.000000
H	0.000000	1.082865	0.000000
H	2.139292	-0.152256	0.000000
H	2.139292	-2.622499	0.000000

H	0.000000	-3.857620	0.000000
H	-2.139292	-2.622499	0.000000
H	-2.139292	-0.152256	0.000000
N	0.000000	0.000000	3.050000
O	0.000000	1.109086	3.050000
O	0.000000	-1.109086	3.050000

$^2B_{2g}$ benzene$^+$:NO_2, path A, gas phase

C	0.000000	1.373310	0.000000
C	1.242304	0.679985	0.000000
C	1.242304	-0.679985	0.000000
C	0.000000	-1.373310	0.000000
C	-1.242304	-0.679985	0.000000
C	-1.242304	0.679985	0.000000
H	0.000000	2.457124	0.000000
H	2.165348	1.243829	0.000000
H	2.165348	-1.243829	0.000000
H	0.000000	-2.457124	0.000000
H	-2.165348	-1.243829	0.000000
H	-2.165348	1.243829	0.000000
N	0.000000	0.000000	3.050000
O	1.091131	0.000000	3.506921
O	-1.091131	0.000000	3.506921

$^2B_{2g}$ benzene$^+$:NO_2, path B, gas phase

C	0.000000	0.693325	0.000000
C	1.242304	0.000000	0.000000
C	1.242304	-1.359970	0.000000
C	0.000000	-2.053295	0.000000
C	-1.242304	-1.359970	0.000000
C	-1.242304	0.000000	0.000000
H	0.000000	1.777139	0.000000
H	2.165348	0.563844	0.000000
H	2.165348	-1.923814	0.000000
H	0.000000	-3.137109	0.000000
H	-2.165348	-1.923814	0.000000
H	-2.165348	0.563844	0.000000
N	0.000000	0.000000	3.050000
O	1.091131	0.000000	3.506921
O	-1.091131	0.000000	3.506921

$^2B_{2g}$ benzene$^+$:NO_2, path D, gas phase

C	0.000000	0.000000	0.000000
C	1.242304	-0.693325	0.000000
C	1.242304	-2.053295	0.000000
C	0.000000	-2.746620	0.000000
C	-1.242304	-2.053295	0.000000
C	-1.242304	-0.693325	0.000000
H	0.000000	1.083814	0.000000
H	2.165348	-0.129481	0.000000
H	2.165348	-2.617139	0.000000
H	0.000000	-3.830434	0.000000
H	-2.165348	-2.617139	0.000000
H	-2.165348	-0.129481	0.000000
N	0.000000	0.000000	3.050000
O	0.000000	1.091131	3.506921
O	0.000000	-1.091131	3.506921

$^2B_{3g}$ benzene$^+$:NO_2, path A, gas phase

C	0.000000	1.434186	0.000000
C	1.189468	0.722597	0.000000
C	1.189468	-0.722597	0.000000
C	0.000000	-1.434186	0.000000
C	-1.189468	-0.722597	0.000000
C	-1.189468	0.722597	0.000000
H	0.000000	2.512882	0.000000
H	2.139069	1.239291	0.000000
H	2.139069	-1.239291	0.000000
H	0.000000	-2.512882	0.000000
H	-2.139069	-1.239291	0.000000
H	-2.139069	1.239291	0.000000
N	0.000000	0.000000	3.050000
O	1.091131	0.000000	3.506921
O	-1.091131	0.000000	3.506921

$^2B_{3g}$ benzene$^+$:NO_2, path B, gas phase

C	0.000000	0.711589	0.000000
C	1.189468	0.000000	0.000000
C	1.189468	-1.445195	0.000000
C	0.000000	-2.156784	0.000000
C	-1.189468	-1.445195	0.000000
C	-1.189468	0.000000	0.000000
H	0.000000	1.790285	0.000000
H	2.139069	0.516693	0.000000
H	2.139069	-1.961888	0.000000
H	0.000000	-3.235480	0.000000
H	-2.139069	-1.961888	0.000000
H	-2.139069	0.516693	0.000000
N	0.000000	0.000000	3.050000
O	1.091131	0.000000	3.506921
O	-1.091131	0.000000	3.506921

$^2B_{3g}$ benzene$^+$:NO_2, path C, gas phase

C	-1.189468	1.434186	0.000000
C	0.000000	0.722597	0.000000
C	0.000000	-0.722597	0.000000
C	-1.189468	-1.434186	0.000000
C	-2.378937	-0.722597	0.000000
C	-2.378937	0.722597	0.000000
H	-1.189468	2.512882	0.000000
H	0.949601	1.239291	0.000000
H	0.949601	-1.239291	0.000000
H	-1.189468	-2.512882	0.000000
H	-3.328537	-1.239291	0.000000
H	-3.328537	1.239291	0.000000
N	0.000000	0.000000	3.050000
O	1.091131	0.000000	3.506921
O	-1.091131	0.000000	3.506921

$^1A_{1g}$ benzene:NO_2^+, path A, dichloromethane

C	0.000000	1.388395	0.000000
C	1.202386	0.694198	0.000000

C	1.202386	-0.694198	0.000000
C	0.000000	-1.388395	0.000000
C	-1.202386	-0.694198	0.000000
C	-1.202386	0.694198	0.000000
H	0.000000	2.471321	0.000000
H	2.140227	1.235661	0.000000
H	2.140227	-1.235661	0.000000
H	0.000000	-2.471321	0.000000
H	-2.140227	-1.235661	0.000000
H	-2.140227	1.235661	0.000000
N	0.000000	0.000000	3.050000
O	1.106725	0.000000	3.050000
O	-1.106725	0.000000	3.050000

$^1A_{1g}$ benzene:NO_2^+, path B, dichloromethane

C	0.000000	0.694198	0.000000
C	1.202386	0.000000	0.000000
C	1.202386	-1.388395	0.000000
C	0.000000	-2.082593	0.000000
C	-1.202386	-1.388395	0.000000
C	-1.202386	0.000000	0.000000
H	0.000000	1.777123	0.000000
H	2.140227	0.541463	0.000000
H	2.140227	-1.929858	0.000000
H	0.000000	-3.165519	0.000000
H	-2.140227	-1.929858	0.000000
H	-2.140227	0.541463	0.000000
N	0.000000	0.000000	3.050000
O	1.106725	0.000000	3.050000
O	-1.106725	0.000000	3.050000

$^1A_{1g}$ benzene:NO_2^+, path C, dichloromethane

C	-1.202386	1.388395	0.000000
C	0.000000	0.694198	0.000000
C	0.000000	-0.694198	0.000000
C	-1.202386	-1.388395	0.000000
C	-2.404772	-0.694198	0.000000
C	-2.404772	0.694198	0.000000
H	-1.202386	2.471321	0.000000
H	0.937841	1.235661	0.000000
H	0.937841	-1.235661	0.000000
H	-1.202386	-2.471321	0.000000
H	-3.342613	-1.235661	0.000000
H	-3.342613	1.235661	0.000000
N	0.000000	0.000000	3.050000
O	1.106725	0.000000	3.050000
O	-1.106725	0.000000	3.050000

$^1A_{1g}$ benzene:NO_2^+, path D, dichloromethane

C	0.000000	0.000000	0.000000
C	1.202386	-0.694198	0.000000
C	1.202386	-2.082593	0.000000
C	0.000000	-2.776791	0.000000
C	-1.202386	-2.082593	0.000000
C	-1.202386	-0.694198	0.000000
H	0.000000	1.082926	0.000000
H	2.140227	-0.152735	0.000000
H	2.140227	-2.624056	0.000000
H	0.000000	-3.859716	0.000000
H	-2.140227	-2.624056	0.000000
H	-2.140227	-0.152735	0.000000
N	0.000000	0.000000	3.050000
O	0.000000	1.106725	3.050000
O	0.000000	-1.106725	3.050000

$^2B_{2g}$ benzene$^+$:NO_2, path A, dichloromethane

C	0.000000	1.372149	0.000000
C	1.240977	0.679492	0.000000
C	1.240977	-0.679492	0.000000
C	0.000000	-1.372149	0.000000
C	-1.240977	-0.679492	0.000000
C	-1.240977	0.679492	0.000000
H	0.000000	2.454487	0.000000
H	2.162116	1.244201	0.000000
H	2.162116	-1.244201	0.000000
H	0.000000	-2.454487	0.000000
H	-2.162116	-1.244201	0.000000
H	-2.162116	1.244201	0.000000
N	0.000000	0.000000	3.050000
O	1.090552	0.000000	3.507337
O	-1.090552	0.000000	3.507337

$^2B_{2g}$ benzene$^+$:NO_2, path B, dichloromethane

C	0.000000	0.692657	0.000000
C	1.240977	0.000000	0.000000
C	1.240977	-1.358983	0.000000
C	0.000000	-2.051640	0.000000
C	-1.240977	-1.358983	0.000000
C	-1.240977	0.000000	0.000000
H	0.000000	1.774995	0.000000
H	2.162116	0.564710	0.000000
H	2.162116	-1.923693	0.000000
H	0.000000	-3.133978	0.000000
H	-2.162116	-1.923693	0.000000
H	-2.162116	0.564710	0.000000
N	0.000000	0.000000	3.050000
O	1.090552	0.000000	3.507337
O	-1.090552	0.000000	3.507337

$^2B_{2g}$ benzene$^+$:NO_2, path D, dichloromethane

C	0.000000	0.000000	0.000000
C	1.240977	-0.692657	0.000000
C	1.240977	-2.051640	0.000000
C	0.000000	-2.744297	0.000000
C	-1.240977	-2.051640	0.000000
C	-1.240977	-0.692657	0.000000
H	0.000000	1.082338	0.000000
H	2.162116	-0.127947	0.000000
H	2.162116	-2.616350	0.000000
H	0.000000	-3.826635	0.000000
H	-2.162116	-2.616350	0.000000
H	-2.162116	-0.127947	0.000000
N	0.000000	0.000000	3.050000

O	0.000000	1.090552	3.507337
O	0.000000	-1.090552	3.507337

$^2B_{3g}$ benzene$^+$:NO_2, path A, dichloromethane

C	0.000000	1.434186	0.000000
C	1.189468	0.722597	0.000000
C	1.189468	-0.722597	0.000000
C	0.000000	-1.434186	0.000000
C	-1.189468	-0.722597	0.000000
C	-1.189468	0.722597	0.000000
H	0.000000	2.512882	0.000000
H	2.139069	1.239291	0.000000
H	2.139069	-1.239291	0.000000
H	0.000000	-2.512882	0.000000
H	-2.139069	-1.239291	0.000000
H	-2.139069	1.239291	0.000000
N	0.000000	0.000000	3.050000
O	1.090552	0.000000	3.507337
O	-1.090552	0.000000	3.507337

$^2B_{3g}$ benzene$^+$:NO_2, path B, dichloromethane

C	0.000000	0.711589	0.000000
C	1.189468	0.000000	0.000000
C	1.189468	-1.445195	0.000000
C	0.000000	-2.156784	0.000000
C	-1.189468	-1.445195	0.000000
C	-1.189468	0.000000	0.000000
H	0.000000	1.790285	0.000000
H	2.139069	0.516693	0.000000
H	2.139069	-1.961888	0.000000
H	0.000000	-3.235480	0.000000
H	-2.139069	-1.961888	0.000000
H	-2.139069	0.516693	0.000000
N	0.000000	0.000000	3.050000
O	1.090552	0.000000	3.507337
O	-1.090552	0.000000	3.507337

$^2B_{3g}$ benzene$^+$:NO_2, path C, dichloromethane

C	-1.189468	1.434186	0.000000
C	0.000000	0.722597	0.000000
C	0.000000	-0.722597	0.000000
C	-1.189468	-1.434186	0.000000
C	-2.378937	-0.722597	0.000000
C	-2.378937	0.722597	0.000000
H	-1.189468	2.512882	0.000000
H	0.949601	1.239291	0.000000
H	0.949601	-1.239291	0.000000
H	-1.189468	-2.512882	0.000000
H	-3.328537	-1.239291	0.000000
H	-3.328537	1.239291	0.000000
N	0.000000	0.000000	3.050000
O	1.090552	0.000000	3.507337
O	-1.090552	0.000000	3.507337

toluene:NO_2^+, path A, gas phase

C	0.000000	1.394976	0.000000
C	1.197315	0.695699	0.000000
C	1.194293	-0.690721	0.000000
C	0.000000	-1.404932	0.000000
C	-1.194293	-0.690721	0.000000
C	-1.197315	0.695699	0.000000
H	0.000000	2.477552	0.000000
H	2.138511	1.231457	0.000000
H	2.135690	-1.228679	0.000000
C	0.000000	-2.908642	0.000000
H	-2.135690	-1.228679	0.000000
H	-2.138511	1.231457	0.000000
H	-0.877969	-3.305364	0.510892
H	0.877969	-3.305364	0.510892
H	0.000000	-3.295299	-1.022326
N	0.000000	0.000000	3.050000
O	1.109086	0.000000	3.050000
O	-1.109086	0.000000	3.050000

toluene:NO_2^+, path B, gas phase

C	0.000000	0.699276	0.000000
C	1.197315	0.000000	0.000000
C	1.194293	-1.386420	0.000000
C	0.000000	-2.100632	0.000000
C	-1.194293	-1.386420	0.000000
C	-1.197315	0.000000	0.000000
H	0.000000	1.781853	0.000000
H	2.138511	0.535758	0.000000
H	2.135690	-1.924379	0.000000
C	0.000000	-3.604342	0.000000
H	-2.135690	-1.924379	0.000000
H	-2.138511	0.535758	0.000000
H	-0.877969	-4.001063	0.510892
H	0.877969	-4.001063	0.510892
H	0.000000	-3.990998	-1.022326
N	0.000000	0.000000	3.050000
O	1.109086	0.000000	3.050000
O	-1.109086	0.000000	3.050000

toluene:NO_2^+, path D, gas phase

C	0.000000	0.000000	0.000000
C	1.197315	-0.699276	0.000000
C	1.194293	-2.085697	0.000000
C	0.000000	-2.799908	0.000000
C	-1.194293	-2.085697	0.000000
C	-1.197315	-0.699276	0.000000
H	0.000000	1.082576	0.000000
H	2.138511	-0.163518	0.000000
H	2.135690	-2.623655	0.000000
C	0.000000	-4.303618	0.000000
H	-2.135690	-2.623655	0.000000
H	-2.138511	-0.163518	0.000000
H	-0.877969	-4.700340	0.510892
H	0.877969	-4.700340	0.510892
H	0.000000	-4.690274	-1.022326
N	0.000000	0.000000	3.050000
O	0.000000	1.109086	3.050000
O	0.000000	-1.109086	3.050000

toluene$^+$:NO_2, path A, gas phase

C	0.000000	1.379696	0.000000
C	-1.233893	0.684496	0.000000
C	-1.235224	-0.674719	0.000000
C	0.000000	-1.399249	0.000000
C	1.235224	-0.674719	0.000000
C	1.233893	0.684496	0.000000
H	0.000000	2.462967	0.000000
H	-2.160484	1.242402	0.000000
H	-2.164140	-1.230548	0.000000
C	0.000000	-2.869281	0.000000
H	2.164140	-1.230548	0.000000
H	2.160484	1.242402	0.000000
H	0.891296	-3.284441	0.469101
H	-0.891296	-3.284441	0.469101
H	0.000000	-3.200748	-1.051312
N	0.000000	0.000000	3.050000
O	1.091131	0.000000	3.506921
O	-1.091131	0.000000	3.506921

toluene$^+$:NO_2, path B, gas phase

C	0.000000	0.695201	0.000000
C	-1.233893	0.000000	0.000000
C	-1.235224	-1.359215	0.000000
C	0.000000	-2.083745	0.000000
C	1.235224	-1.359215	0.000000
C	1.233893	0.000000	0.000000
H	0.000000	1.778472	0.000000
H	-2.160484	0.557906	0.000000
H	-2.164140	-1.915044	0.000000
C	0.000000	-3.553777	0.000000
H	2.164140	-1.915044	0.000000
H	2.160484	0.557906	0.000000
H	0.891296	-3.968937	0.469101
H	-0.891296	-3.968937	0.469101
H	0.000000	-3.885244	-1.051312
N	0.000000	0.000000	3.050000
O	1.091131	0.000000	3.506921
O	-1.091131	0.000000	3.506921

toluene$^+$:NO_2, path D, gas phase

C	0.000000	0.000000	0.000000
C	-1.233893	-0.695201	0.000000
C	-1.235224	-2.054416	0.000000
C	0.000000	-2.778946	0.000000
C	1.235224	-2.054416	0.000000
C	1.233893	-0.695201	0.000000
H	0.000000	1.083271	0.000000
H	-2.160484	-0.137295	0.000000
H	-2.164140	-2.610244	0.000000
C	0.000000	-4.248978	0.000000
H	2.164140	-2.610244	0.000000
H	2.160484	-0.137295	0.000000
H	0.891296	-4.664138	0.469101
H	-0.891296	-4.664138	0.469101
H	0.000000	-4.580444	-1.051312
N	0.000000	0.000000	3.050000
O	0.000000	1.091131	3.506921
O	0.000000	-1.091131	3.506921

toluene:NO_2^+, path A, dichloromethane

C	0.000000	1.396226	0.000000
C	1.198090	0.696206	0.000000
C	1.195076	-0.691235	0.000000
C	0.000000	-1.406168	0.000000
C	-1.195076	-0.691235	0.000000
C	-1.198090	0.696206	0.000000
H	0.000000	2.478923	0.000000
H	2.139474	1.231874	0.000000
H	2.136549	-1.229057	0.000000
C	0.000000	-2.909928	0.000000
H	-2.136549	-1.229057	0.000000
H	-2.139474	1.231874	0.000000
H	-0.879119	-3.305951	0.509131
H	0.879119	-3.305951	0.509131
H	0.000000	-3.295246	-1.022778
N	0.000000	0.000000	3.050000
O	1.106725	0.000000	3.050000
O	-1.106725	0.000000	3.050000

toluene:NO_2^+, path B, dichloromethane

C	0.000000	0.700020	0.000000
C	1.198090	0.000000	0.000000
C	1.195076	-1.387441	0.000000
C	0.000000	-2.102374	0.000000
C	-1.195076	-1.387441	0.000000
C	-1.198090	0.000000	0.000000
H	0.000000	1.782717	0.000000
H	2.139474	0.535668	0.000000
H	2.136549	-1.925263	0.000000
C	0.000000	-3.606134	0.000000
H	-2.136549	-1.925263	0.000000
H	-2.139474	0.535668	0.000000
H	-0.879119	-4.002157	0.509131
H	0.879119	-4.002157	0.509131
H	0.000000	-3.991451	-1.022778
N	0.000000	0.000000	3.050000
O	1.106725	0.000000	3.050000
O	-1.106725	0.000000	3.050000

toluene:NO_2^+, path D, dichloromethane

C	0.000000	0.000000	0.000000
C	1.198090	-0.700020	0.000000
C	1.195076	-2.087461	0.000000
C	0.000000	-2.802394	0.000000
C	-1.195076	-2.087461	0.000000
C	-1.198090	-0.700020	0.000000
H	0.000000	1.082697	0.000000
H	2.139474	-0.164352	0.000000
H	2.136549	-2.625283	0.000000
C	0.000000	-4.306154	0.000000
H	-2.136549	-2.625283	0.000000

H	-2.139474	-0.164352	0.000000
H	-0.879119	-4.702177	0.509131
H	0.879119	-4.702177	0.509131
H	0.000000	-4.691472	-1.022778
N	0.000000	0.000000	3.050000
O	0.000000	1.106725	3.050000
O	0.000000	-1.106725	3.050000

toluene$^+$:NO_2, path A, dichloromethane

C	0.000000	1.378137	0.000000
C	-1.233077	0.683871	0.000000
C	-1.234865	-0.674590	0.000000
C	0.000000	-1.396698	0.000000
C	1.234865	-0.674590	0.000000
C	1.233077	0.683871	0.000000
H	0.000000	2.460205	0.000000
H	-2.158096	1.242476	0.000000
H	-2.161613	-1.232276	0.000000
C	0.000000	-2.865676	0.000000
H	2.161613	-1.232276	0.000000
H	2.158096	1.242476	0.000000
H	0.891875	-3.273543	0.473382
H	-0.891875	-3.273543	0.473382
H	0.000000	-3.196874	-1.049169
N	0.000000	0.000000	3.050000
O	1.090552	0.000000	3.507337
O	-1.090552	0.000000	3.507337

toluene$^+$:NO_2, path B, dichloromethane

C	0.000000	0.694267	0.000000
C	-1.233077	0.000000	0.000000
C	-1.234865	-1.358461	0.000000
C	0.000000	-2.080568	0.000000
C	1.234865	-1.358461	0.000000
C	1.233077	0.000000	0.000000
H	0.000000	1.776334	0.000000
H	-2.158096	0.558605	0.000000
H	-2.161613	-1.916147	0.000000
C	0.000000	-3.549547	0.000000
H	2.161613	-1.916147	0.000000
H	2.158096	0.558605	0.000000
H	0.891875	-3.957414	0.473382
H	-0.891875	-3.957414	0.473382
H	0.000000	-3.880745	-1.049169
N	0.000000	0.000000	3.050000
O	1.090552	0.000000	3.507337
O	-1.090552	0.000000	3.507337

toluene$^+$:NO_2, path D, dichloromethane

C	0.000000	0.000000	0.000000
C	-1.233077	-0.694267	0.000000
C	-1.234865	-2.052728	0.000000
C	0.000000	-2.774835	0.000000
C	1.234865	-2.052728	0.000000
C	1.233077	-0.694267	0.000000
H	0.000000	1.082067	0.000000
H	-2.158096	-0.135661	0.000000
H	-2.161613	-2.610414	0.000000
C	0.000000	-4.243813	0.000000
H	2.161613	-2.610414	0.000000
H	2.158096	-0.135661	0.000000
H	0.891875	-4.651680	0.473382
H	-0.891875	-4.651680	0.473382
H	0.000000	-4.575011	-1.049169
N	0.000000	0.000000	3.050000
O	0.000000	1.090552	3.507337
O	0.000000	-1.090552	3.507337

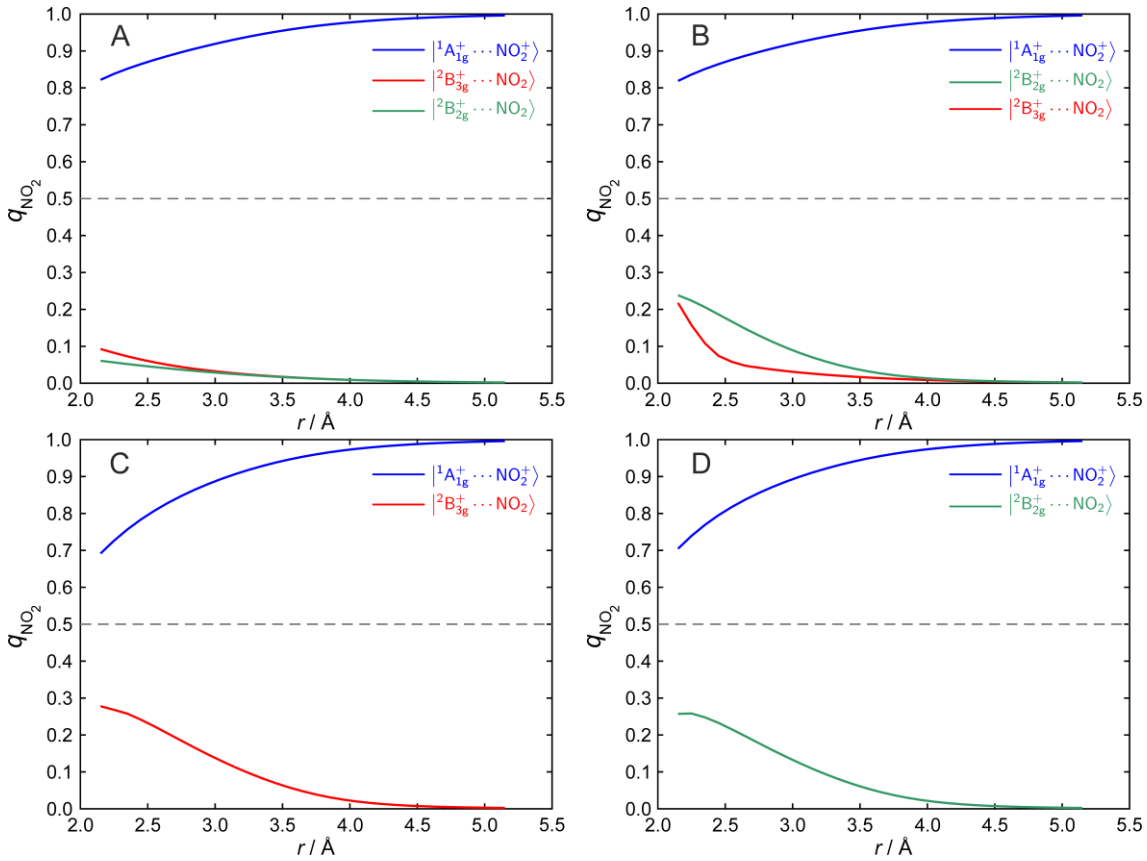

Figure S1. CM5 net atomic charge of NO_2 as a function of the distance between interacting units for paths A, B, C, and D of benzene in the gas phase.

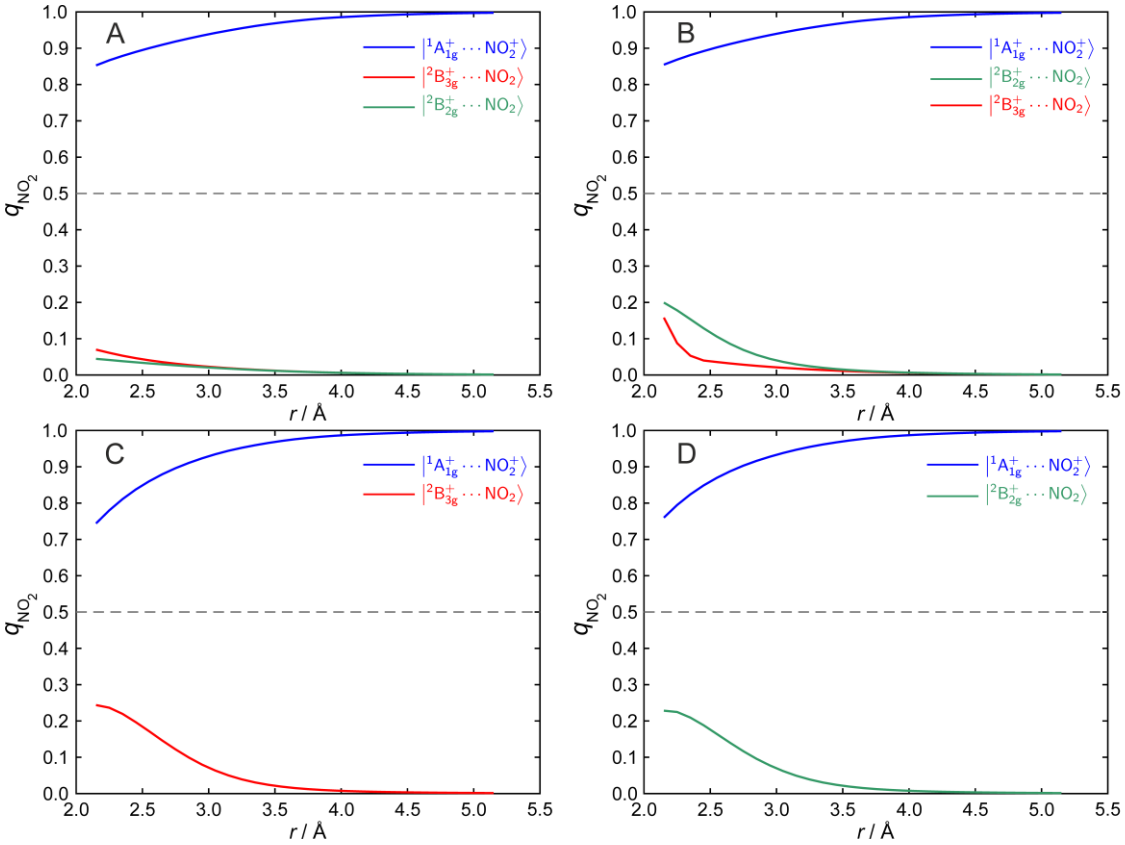

Figure S2. CM5 net atomic charge of NO_2 as a function of the distance between interacting units for paths A, B, C, and D of benzene in dichloromethane.

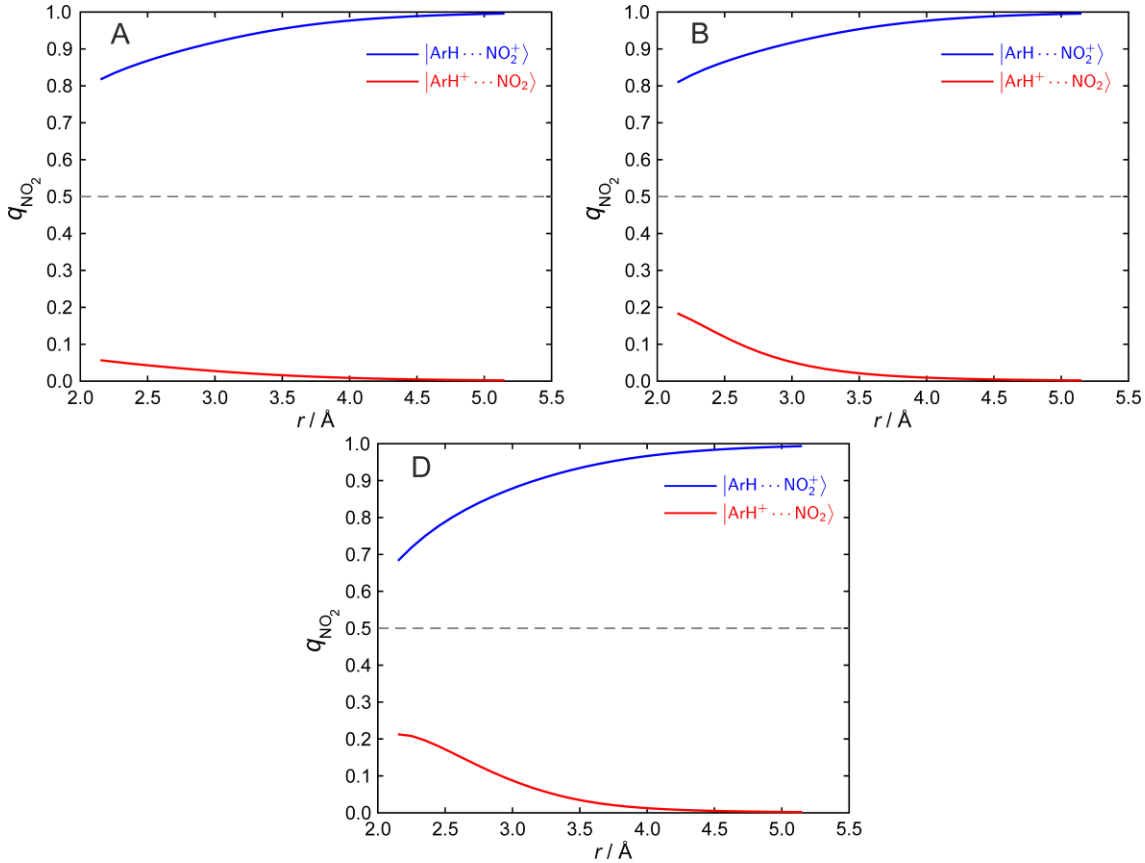

Figure S3. CM5 net atomic charge of NO_2 as a function of the distance between interacting units for paths A, B, and D of toluene in the gas phase.

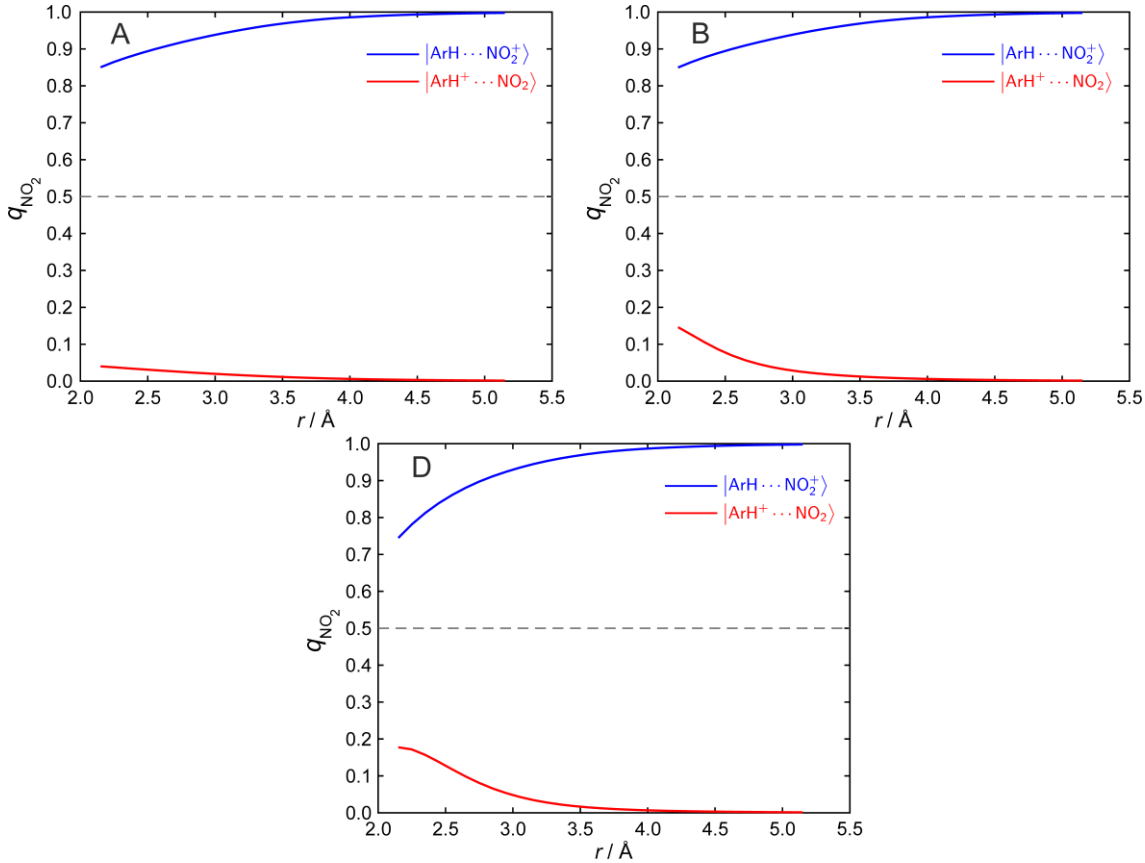

Figure S4. CM5 net atomic charge of NO_2 as a function of the distance between interacting units for paths A, B, and D of toluene in dichloromethane.

Table S1. Critical points for benzene / NO_2, path A, gas phase; *r* is given in Å, E_{int} (vs neutral NO_2 and benzene$^+$) is expressed in kcal/mol.

r	$E_{int}(A_{1g})$	E_{int} (B_{2g})	E_{int} (B_{3g})
3.05[a]	-3.8	+0.2	-0.1
3.35[b]	-2.8	-0.3	-0.3
3.25[c]	-3.4	-0.2	-0.3

[a]Minimum for A_{1g} profile. [b]Minimum for B_{2g} profile. [c]Minimum for B_{3g} profile.

Table S2. Critical points for benzene / NO_2, path B, gas phase; *r* is given in Å, E_{int} (vs neutral NO_2 and benzene$^+$) is expressed in kcal/mol.

r	$E_{int}(A_{1g})$	E_{int} (B_{2g})	E_{int} (B_{3g})
3.05[a]	-3.4	-1.1	+0.3
3.35[b]	-2.5	-0.8	-0.1

[a]Minimum for A_{1g} and B_{2g} profiles. [b]Minimum for B_{3g} profile.

Table S3. Critical points for benzene / NO_2, path C, gas phase; *r* is given in Å, E_{int} (vs neutral NO_2 and benzene$^+$) is expressed in kcal/mol.

r	$E_{int}(A_{1g})$	E_{int} (B_{3g})
2.85[a]	-5.8	-4.6
2.15[b]	+19.9	-8.5

[a]Minimum for A_{1g} profile. [b]Interaction energy is a strictly increasing function of *r* for B_{3g} profile.

Table S4. Critical points for benzene / NO_2, path D, gas phase; *r* is given in Å, E_{int} (vs neutral NO_2 and benzene$^+$) is expressed in kcal/mol.

r		$E_{int}(A_{1g})$	E_{int} (B_{2g})
2.85[a]		-5.0	-4.9
2.15[b]		+22.6	-8.8

[a]Minimum for A_{1g} profile. [b]Interaction energy is a strictly increasing function of *r* for B_{2g} profile.

Table S5. Critical points for toluene / NO_2, path A, gas phase; *r* is given in Å, E_{int} (vs neutral NO_2 and toluene$^+$) is expressed in kcal/mol.

r	$E_{int}(ArH^{\cdots}NO_2^+)$	$E_{int}(ArH^{+\cdots}NO_2)$
3.05[a]	+5.8	0.0
3.35[b]	+7.0	-0.4

[a]Minimum for $ArH^{\cdots}NO_2^+$ profile. [b]Minimum for $ArH^{+\cdots}NO_2$ profile.

Table S6. Critical points for toluene / NO_2, path B, gas phase; *r* is given in Å, E_{int} (vs neutral NO_2 and toluene$^+$) is expressed in kcal/mol.

r	$E_{int}(ArH^{\cdots}NO_2^+)$	$E_{int}(ArH^{+\cdots}NO_2)$
3.05[a]	+6.0	-0.5
3.35[b]	+6.2	-0.6

[a]Minimum for $ArH^{\cdots}NO_2^+$ profile. [b]Minimum for $ArH^{+\cdots}NO_2$ profile.

Table S7. Critical points for toluene / NO_2, path D, gas phase; *r* is given in Å, E_{int} (vs neutral NO_2 and toluene$^+$) is expressed in kcal/mol.

r	E_{int}(ArH···NO_2^+)	E_{int}(ArH$^+$···NO_2)
2.85[a]	+3.8	-3.4
2.15[b]	+30.1	-5.4

[a]Minimum for ArH···NO_2^+ profile. [b]Interaction energy is a strictly increasing function of *r* for ArH$^+$···NO_2 profile.

Table S8. Critical points for benzene / NO_2, path A, dichloromethane; *r* is given in Å, E_{int} (vs NO_2^+ and neutral benzene) is expressed in kcal/mol.

r	E_{int}(A_{1g})	E_{int} (B_{2g})	E_{int} (B_{3g})
3.35[a]	-2.1	+7.9	+8.2
3.75[b]	-1.9	+7.7	+8.1
3.85[c]	-1.8	+7.7	+8.1

[a]Minimum for A_{1g} profile. [b]Minimum for B_{3g} profile. [c]Minimum for B_{2g} profile.

Table S9. Critical points for benzene / NO_2, path AB dichloromethane; *r* is given in Å, E_{int} (vs NO_2^+ and neutral benzene) is expressed in kcal/mol.

r	E_{int}(A_{1g})	E_{int} (B_{2g})	E_{int} (B_{3g})
3.25[a]	-1.9	+7.7	+8.4
3.55[b]	-1.9	+7.7	+8.1
3.65[c]	-1.8	+7.7	+8.1

[a]Minimum for A_{1g} profile. [b]Minimum for B_{2g} profile. [c]Minimum for B_{3g} profile.

Table S10. Critical points for benzene / NO_2, path C, dichloromethane; *r* is given in Å, E_{int} (vs NO_2^+ and neutral benzene) is expressed in kcal/mol.

r	E_{int}(A_{1g})	E_{int} (B_{3g})
3.05[a]	-2.9	+6.8
2.15[b]	+27.1	+2.4

[a]Minimum for A_{1g} profile. [b]Interaction energy is a strictly increasing function of *r* for B_{3g} profile.

Table S11. Critical points for benzene / NO_2, path D, dichloromethane; *r* is given in Å, E_{int} (vs NO_2^+ and neutral benzene) is expressed in kcal/mol.

r	E_{int}(A_{1g})	E_{int} (B_{2g})
3.15[a]	-2.5	+6.6
2.15[b]	+29.3	+2.0

[a]Minimum for A_{1g} profile. [b]Interaction energy is a strictly increasing function of *r* for B_{2g} profile.

Table S12. Critical points for toluene / NO_2, path A, dichloromethane; *r* is given in Å, E_{int} (vs neutral NO_2 and toluene$^+$) is expressed in kcal/mol.

r	E_{int}(ArH···NO_2^+)	E_{int}(ArH$^+$···NO_2)
3.35[a]	-2.4	-0.7
3.75[b]	-2.0	-0.8

[a]Minimum for ArH···NO_2^+ profile. [b]Minimum for ArH$^+$···NO_2 profile.

Table S13. Critical points for toluene / NO_2, path B, dichloromethane; *r* is given in Å, E_{int} (vs neutral NO_2 and toluene$^+$) is expressed in kcal/mol.

r	E_{int}(ArH···NO_2^+)	E_{int}(ArH$^+$···NO_2)
3.15[a]	-2.4	-0.6
3.55[b]	-2.2	-0.8

[a]Minimum for ArH···NO_2^+ profile. [b]Minimum for ArH$^+$···NO_2 profile.

Table S14. Critical points for toluene / NO_2, path D, dichloromethane; *r* is given in Å, E_{int} (vs neutral NO_2 and toluene$^+$) is expressed in kcal/mol.

r	E_{int}(ArH···NO_2^+)	E_{int}(ArH$^+$···NO_2)
3.05[a]	-3.1	-1.7
2.15[b]	+27.6	-3.7

[a]Minimum for ArH···NO_2^+ profile. [b]Interaction energy is a strictly increasing function of *r* for ArH$^+$···NO_2 profile.