Supplementary information to "Solvation in nitration of benzene and the valence electronic structure of Wheland intermediate"

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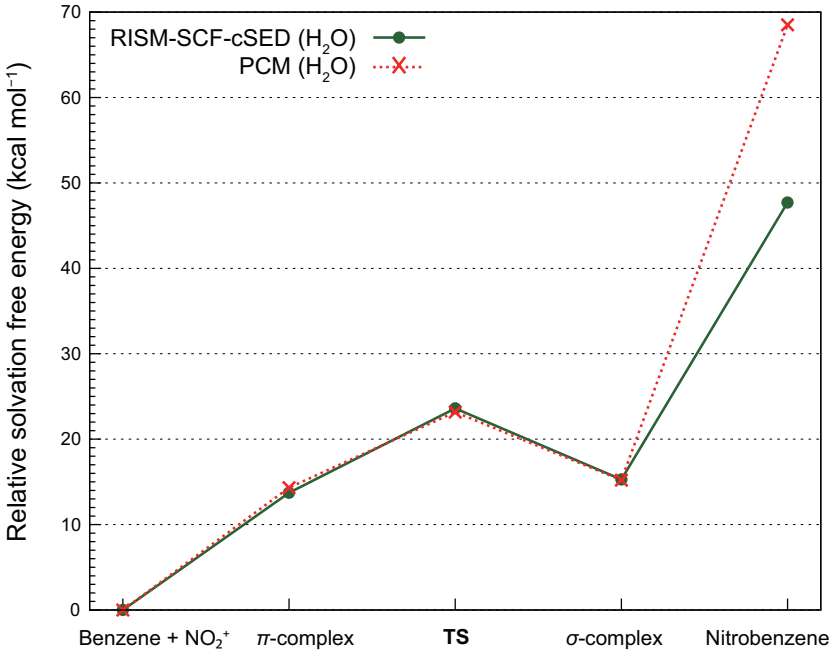

Figure S1: Relative solvation free energies (kcal mol^{-1}) in the process of nitration of benzene in the H_2O solution evaluated with the RISM-SCF-cSED and PCM. Solvation free energy in the PCM was evaluated as $E_{\rm el} + E_{\rm disp} + E_{\rm rep} + E_{\rm cav} - \langle\Psi|H|\Psi\rangle$ where Ψ is the wave function in solution.

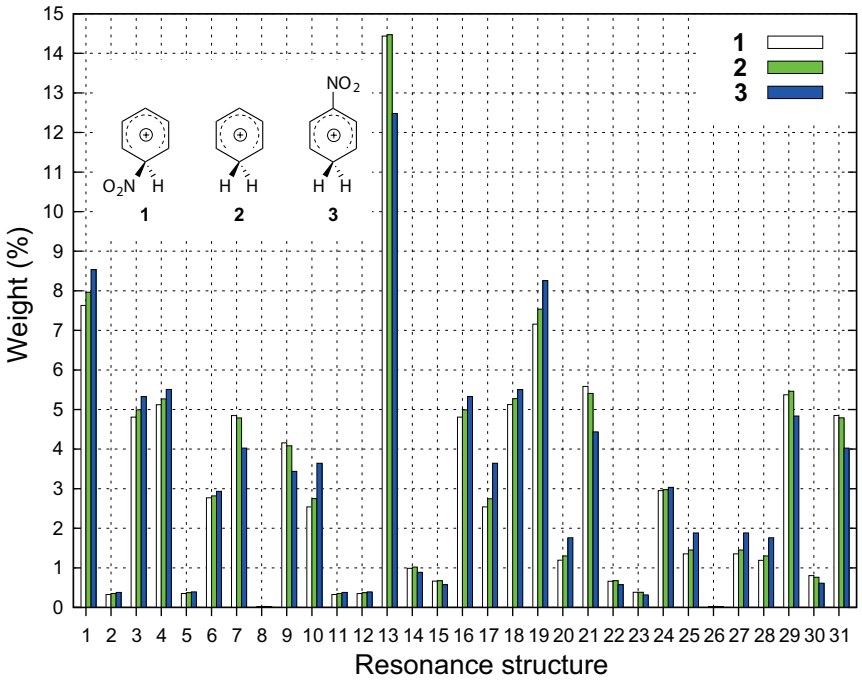

Figure S2: Weights of resonance structures in the three σ-complexes (**1**, **2** and **3** shown in the figure) calculated with M06-2X/6-311G(d,p) in the gas phase.

Table S1: Weights (%) of resonance structures in the σ-complex (**1**) calculated by various methods with 6-311G(d,p).[a]

Structure	Degeneracy	Hartree-Fock	M06-2X	B3LYP	BLYP
1	4	7.00	7.63	7.68	7.72
2	4	0.22	0.33	0.34	0.36
3	4	4.75	4.81	4.80	4.75
4	4	4.21	5.12	5.31	5.50
5	4	0.20	0.35	0.38	0.42
6	4	2.57	2.77	2.83	2.85
7	2	5.35	4.85	4.71	4.61
8	2	0.01	0.02	0.02	0.03
9	2	4.82	4.16	4.01	3.88
10	2	1.87	2.54	2.70	2.84
11	2	0.22	0.33	0.34	0.36
12	2	0.20	0.35	0.38	0.42
13	2	17.82	14.44	13.62	12.92
14	2	0.83	0.99	0.98	0.99
15	2	0.50	0.66	0.68	0.71
16	2	4.75	4.81	4.80	4.75
17	2	1.87	2.54	2.70	2.84
18	2	4.21	5.13	5.31	5.50
19	2	7.91	7.16	6.93	6.67
20	1	1.05	1.19	1.22	1.23
21	2	5.79	5.58	5.56	5.53
22	2	0.50	0.66	0.68	0.71
23	2	0.27	0.38	0.40	0.42
24	2	2.27	2.95	3.13	3.30
25	1	0.83	1.35	1.50	1.64
26	2	0.01	0.02	0.02	0.03
27	2	0.83	1.35	1.50	1.64
28	2	1.05	1.19	1.22	1.23
29	1	7.41	5.37	4.92	4.53
30	1	0.78	0.80	0.82	0.83
31	2	5.35	4.85	4.71	4.61
Others		4.54	5.30	5.79	6.16
Total		100.00	100.00	100.00	100.00

[a] Geometry was fixed at the one optimised by M06-2X.