Supporting Information for:

Aromatic Amine Nitration Mechanisms: Reactivity Governed by Resonance-Assisted Hydrogen Bonds

Tianlong Wu[a], Zhe Wu[a],Guo-Ping Lu[a], Hua Guan[a], Dabin Liu[a], Yingzhe Liu[b], Baojing Zhou[a]*

[a] School of Chemistry and Chemical Engineering, Nanjing University of Science & Technology, Nanjing, 210094, China

[b] Xi'an Modern Chemistry Research Institute, Xi'an, 710065, China

* Corresponding author: bzhou@mail.njust.edu.cn

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1. Structural properties of substrates

Table S1 Structural and electronic features of substrate amino groups: H-N-H bond angle, hybridization of N atom, electron density (10^{-4} a.u.) at hydrogen bond critical point and QTAIM charges of N atom.

Substrate	∠H-N-H	hybridization	ρ_{BCP}	charges
3-AT	112°	sp3	-	-1.14
ANPZ	120°	sp2	249.90	-1.26
LLM-105[a]	122°	sp2	251.23/235.30	-1.26
TATB	121°	sp2	414.50	-1.28
TATB-Ac·	-	sp2	210.54	-1.23

a. The amino groups of LLM-105 contain two asymmetric hydrogen atoms.

Table S2 The NICS(1)zz value (ppm) at the center of the aromatic ring and EDDB[k] value (e^-) of the amino group for different substrates obtained from DFT.

Substrate	**NICS(1)zz**	**EDDB[k]**
3-AT	-8.88	0.42
ANPZ	-5.45	0.81
LLM-105	-6.67	0.86
TATB	-5.03	0.89
TATB-Ac	-9.23	-
Benzene	-10.10	-

2. Thermodynamic parameters for stepwise and synergistic mechanisms

Table S3 Computed single-point electronic energies (E^{M06-2X}_{sp}), thermal correction to the Gibbs free energies (G^{M06-2X}_{corr}) at 298.15 K and solvation free energies (ΔG^{M05-2X}_{solv}) for different states along the stepwise nitration pathway of five substrates and benzene in the formamide (ε = 108.9) and total changes of the solution-phase Gibbs free energy (ΔG^{Total}_{soln}) from reactants to other states including the reactant complex (RC), TS and σ-complex (Fig. 2, 5a, 6, 9a in the text). The unit is kcal/mol.

Substrate	State	E^{M06-2X}_{sp}	G^{M06-2X}_{corr}	ΔG^{M05-2X}_{solv}	ΔG^{Total}_{soln}
3-AT	reactants (step 1)	-315213.37	25.57	-91.78	-
	RC	-315232.41	33.73	-77.40	1.61
	TS	-315235.24	34.55	-74.48	2.52
	σ-complex	-315241.28	37.29	-79.57	-5.87
	reactants (step 2)	-491178.04	30.30	-141.06	-
	products	-491341.70	42.21	-5.21	-17.79
ANPZ	reactants	-620482.34	43.44	-81.29	-
	RC	-620496.97	53.70	-71.21	3.82
	TS	-620499.90	54.45	-62.05	10.81
	σ-complex	-620501.17	56.25	-65.79	7.59
LLM-105	reactants	-667648.55	45.90	-72.86	-
	RC	-667687.54	57.06	-61.16	-10.78
	TS	-667666.86	57.05	-58.74	12.31
	σ-complex	-667665.90	57.76	-61.03	11.69
TATB	reactants	-763418.57	68.79	-72.86	-
	RC	-763440.15	77.13	-62.39	-4.67
	TS	-763434.83	78.14	-51.06	12.99
	σ-complex	-763445.71	79.85	-51.97	2.92
TATB-Ac	reactants	-1050773.27	68.79	-82.98	-
	RC	-1050788.64	141.47	-74.16	1.77
	TS	-1050794.16	142.14	-50.23	20.84
	products	-1050799.84	138.75	-65.92	-3.90
Benzene	reactants	-274188.70	41.06	-76.30	-
	RC	-274207.72	49.54	-62.56	1.30
	TS	-274213.11	49.70	-50.35	8.29
	σ-complex	-274218.21	50.76	-62.96	-8.36

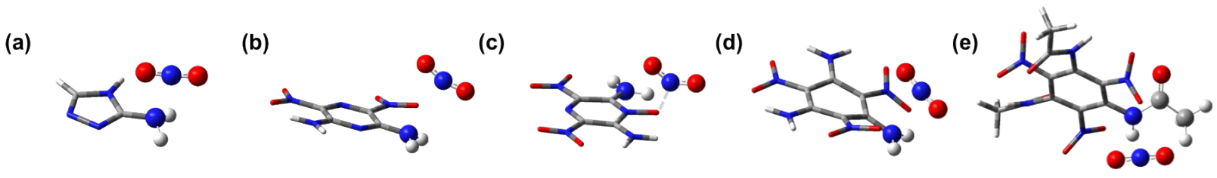

Figure S1 Structures of reactant complexes (RC) formed from (a) 3-AT, (b) ANPZ, (c) LLM-105, (d) TATB, and (e) TATB-Ac with NO_2^+ in the stepwise mechanism of aromatic amine nitration.

Table S4 Computed single-point electronic energies (E_{sp}^{M06-2X}), thermal correction to the Gibbs free energies (G_{corr}^{M06-2X}) at 298.15 K and solvation free energies (ΔG_{solv}^{M05-2X}) for different states along the synergistic nitration pathway of five substrates in the formamide (ε = 108.9) and total changes of the solution-phase Gibbs free energy (ΔG_{soln}^{Total}) from reactants to other states including the reactant complex (RC), TS and products (Fig. 3, 5b, 7, 9b in the text). The unit is kcal/mol.

Substrate	State	E_{sp}^{M06-2X}	G_{corr}^{M06-2X}	ΔG_{solv}^{M05-2X}	ΔG_{soln}^{Total}
3-AT	reactants	-491307.81	28.64	-5.69	-
	RC	-491316.67	41.76	-3.64	4.42
	TS	-491303.70	42.84	-6.04	16.06
	products	-491341.70	42.21	-5.21	-21.73
ANPZ	reactants	-796576.78	46.51	4.80	-
	RC	-796584.19	59.59	4.32	3.29
	TS1	-796560.87	61.98	-3.44	21.25
	TS2	-796553.90	61.76	-7.50	23.93
	products	-796595.34	60.85	0.13	-10.78
LLM-105	reactants	-843742.98	48.97	5.98	-
	RC	-843752.16	62.17	6.49	2.64
	TS1	-843721.24	63.46	-3.55	24.82
	TS2	-843721.74	63.81	-4.19	24.02
	products	-843764.22	64.10	1.30	-12.67
TATB	reactants	-939513.00	71.86	13.23	-
	RC	-939520.37	83.67	10.99	0.31
	TS	-939493.15	87.12	4.29	24.28
	products	-939533.96	86.72	6.53	-14.69
TATB-Ac	reactants	-1226867.71	134.33	3.11	-
	RC	-1226871.15	146.12	2.81	6.15
	TS	-1226843.94	148.55	-4.54	28.45
	products	-1226890.61	148.76	2.19	-11.28

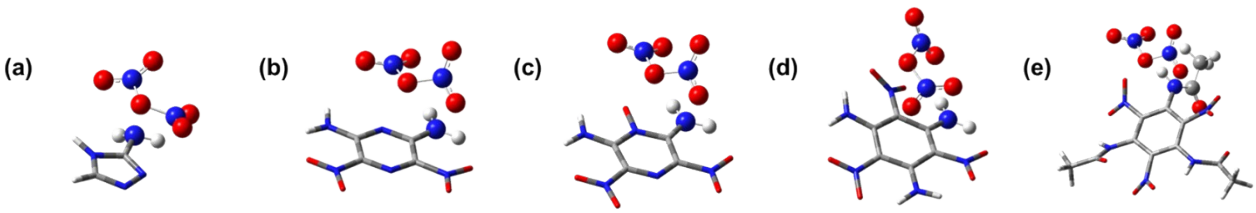

Figure S2 Structures of reactant complex (RC) formed from (a) 3-AT, (b) ANPZ, (c) LLM-105, (d) TATB, (e) TATB-Ac with N_2O_5 in the synergistic mechanism of aromatic amine nitration.

Table S5 The three lowest frequencies (at 298.15 K) obtained from TS geometry optimization for each nitration pathway.

Nitration type	Substrate	Freq[1]	Freq[2]	Freq[3]
Stepwise mechanism	3-AT	-210.27	38.14	47.04
	ANPZ	-319.69	37.36	50.38
	LLM-105	-191.56	48.09	51.81
	TATB	-351.22	23.80	33.53
	TATB-Ac	-187.70	34.99	36.84
	Benzene	-199.28	18.87	125.13
Synergistic mechanism	3-AT	-319.95	39.15	64.12
	ANPZ (TS1)	-318.79	30.23	35.08
	ANPZ (TS2)	-381.67	28.67	34.47
	LLM-105 (TS1)	-415.34	29.39	35.27
	LLM-105 (TS2)	-389.59	31.40	42.09
	TATB	-349.06	26.56	28.81
	TATB-Ac	-317.82	24.45	31.38

Table S6 Comparison of barriers ($\Delta G^{\ddagger}$) and reaction Gibbs free energy changes ($\Delta_r G_m$) calculated at the M06-2X/def2-TZVP and DLPNO-CCSD(T)/def2-TZVPP levels. The unit is kcal/mol.

Nitration type	Substrate	$\Delta G^{\ddagger}$ M06-2X	$\Delta G^{\ddagger}$ DLPNO-CCSD(T)	$\Delta_r G_m$ M06-2X	$\Delta_r G_m$ DLPNO-CCSD(T)
Stepwise mechanism	3-AT	2.51	5.79	-5.87	-2.06
	ANPZ	10.81	12.33	7.59	8.73
	TATB	12.99	9.98	2.92	4.59
Synergistic mechanism	3-AT	16.06	16.28	-21.73	-20.11
	ANPZ (TS1)	21.25	21.48	-10.78	-10.52
	ANPZ (TS2)	23.93	23.89		
	TATB	24.28	23.01	-14.69	-13.66

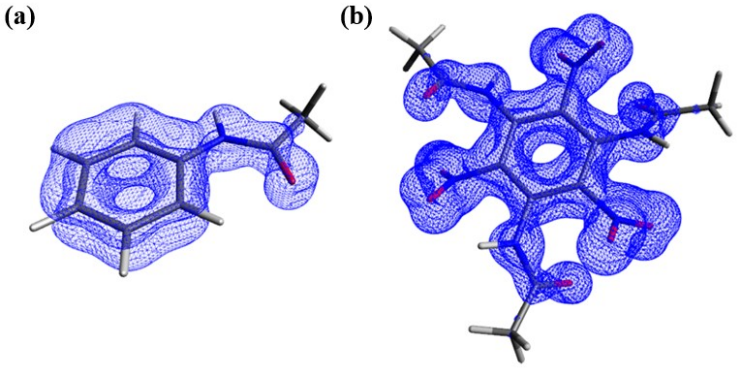

Figure S3 Comparison of structures of (a) acetanilide and (b) TATB-Ac. Blue mesh represents the delocalized π-electron density computed from DFT.

3. DFT optimized cartesian coordinates for substrates

The optimized Cartesian coordinates are provided in a separate compressed archive. (Structures.zip)