SUPPORTING INFORMATION

Keto ⇌ Enol, Imine ⇌ Enamine, and Nitro ⇌ *aci*-Nitro Tautomerism and Their Interrelationship in Substituted Nitroethylenes. Keto, Imine, Nitro, and Vinyl Substituent Effects and the Importance of H-bonding.

by

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Supporting Material.

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Table 1s. Absolute Energies (in −hartrees) of Nitrovinylalcohol, **1**, its Conformers, Tautomers, Transiton Structures and Anions.[a]

Structure		HF/6-31G*	MP2/6-31G*	MP4/6-31G*[b]	B3LYP/6-31G*	B3LYP/6-311+G**[c]	G2MP2	ZPE[d]
1Aa	C_s	356.37129 (0)	357.36069	357.39829	358.32154	358.44111	357.83458	37.6
1Ab	C_s	356.35286 (0)	357.34116	357.37938	358.29974	358.42211	--	37.1
1Ac	C_s	356.36242 (0)	357.34887	357.38704	358.30777	358.42917	--	37.1
1Ad	C_s	356.36090 (0)	357.34721	357.38535	358.30635	358.42864	--	37.0
1Ba	C_s	356.35703 (0)	357.35329	357.38967	358.31603	358.43458	357.82638	37.0
1Bb	C_s	356.34941 (0)	357.34040	357.37866	358.30104	358.42054	--	36.6
1Bc	C_s	356.35520 (0)	357.34473	357.38352	358.30507	358.42576	--	36.5
1Bd	C_s	356.33550 (1)	357.33056	357.36903	358.29253	358.41410	--	35.9
1Ca	C_1	356.37765 (0)	357.36617	357.40566	358.31824	358.43482	357.83390	36.5
1Cb	C_1	356.37488 (0)	357.36492	357.40411	358.31561	358.43260	--	36.7
1Da⁻	C_s	355.81821 (0)	356.80925	356.84379	357.76834	357.90529	357.30469	28.3
1Db	C_s	355.82913 (0)	356.81826	356.85287	357.77741	357.91486	357.31398	28.9
1E	C_s	356.34804 (1)	357.34911	357.38392	358.31385	358.43320	357.82827	34.5
1Aa (ts)	C_1	356.34669 (1)	357.33789	357.37643	358.29258	358.41670	--	36.7
1Ac (ts)	C_1	356.34531 (1)	357.33609	357.37469	358.29129	358.41494	--	36.6

[a] Values in parentheses are the number of imaginary frequencies.

[b] Using MP2/6-31G* geometries.

[c] Using B3LYP/6-31G* geometries.

[d] Zero Point Vibrational Energies at HF/6-31G*, scaled by 0.8929.

Table 2s. Absolute Energies (in −hartrees) of Nitrovinylamine, **2**, its Conformers, Tautomers, Transtion Structures and Anions. [a]

Structure		HF/6-31G*	MP2/6-31G*	MP4/6-31G*[b]	B3LYP/6-31G*	B3LYP/6-311+G**[c]	G2MP2	ZPE[d]
2Aa	C_s	336.54755 (0)	337.52181	337.56267	338.46034	338.57464	337.97065	44.5
2Ab	C_1	336.54323 (0)	337.51516	337.55674	338.45316	338.56775	--	44.1
2Ac	C_s	336.54319 (1)	337.51482	337.55606	338.45314	338.56784	--	43.8
2Ba	C_s	336.51574 (0)	337.49950	337.53963	338.43904	338.55396	337.95040	44.5
2Bb	C_s	336.51610 (0)	337.49230	337.53621	338.42979	338.54434	--	44.4
2Bc	C_s	336.49502 (1)	337.47515	337.51896	338.41449	338.53120	--	43.6
2Ca	C_1	336.54003 (0)	337.51459	337.55875	338.44398	338.55487	337.95896	44.5
2Cb	C_1	336.53573 (0)	337.51190	337.55567	338.43998	338.55148	--	44.4
2Da	C_s	335.95711 (0)	336.93604	336.97493	337.87329	338.00548	337.41216	36.2
2Db	C_s	335.97255 (0)	336.94944	336.98845	337.88666	338.01924	337.42509	36.3
2E	C_s	336.50763 (1)	337.49748	337.53609	338.43860	338.55360	337.95273	41.8
2Aa (ts)	C_1	336.52477 (1)	337.50170	337.54411	338.43426	338.55120	--	44.0
2Ab (ts)	C_1	336.52319 (1)	337.49965	337.54221	338.43268	338.54904	--	43.9

[a] Values in parentheses are the number of imaginary frequencies.

[b] Using MP2/6-31G* geometries.

[c] Using B3LYP/6-31G* geometries.

[d] Zero Point Vibrational Energies at HF/6-31G*, scaled by 0.8929.

Table 3s. Absolute Energies (in −hartrees) of 1-Nitropropene, **3**, its Conformers, Tautomers, Transition Structures and Anions.[a]

Structure		HF/6-31G*	MP2/6-31G*	MP4/6-31G*[b]	B3LYP/6-31G*	B3LYP/6-311+G**	G2MP2	ZPE[c]
3Ac	C_s	320.54667 (0)	321.48899	321.53577	322.41067	322.51157	321.91539	50.6
3Aa	C_s	320.54169 (0)	321.48544	321.53231	322.40669	322.50720	321.91168	50.7
3Ab	C_s	320.54120 (1)	321.48438	321.53118	322.40661	322.50740	--	50.6
3Ba	C_1	320.51239 (0)	321.45489	321.50247	322.38306	322.49115	321.89321	50.7
3Bb	C_1	320.51782 (0)	321.45898	321.50658	322.38732	322.49574	--	50.6
3Ca	C_1	320.54121 (0)	321.48403	321.53107	322.40236	322.50557	321.91069	51.0
3Cb	C_1	320.53758 (0)	321.48152	321.52838	322.39907	322.50233	--	50.9
3Da	C_s	319.95544 (0)	320.90327	320.94546	321.82878	321.95437	321.36340	42.6
3Db	C_s	319.96034 (0)	320.90571	320.94803	321.83257	321.95785	321.36532	42.4
3E	C_1	320.44925 (1)	321.41821	321.45982	322.34729	322.45137	321.85219	47.8
3Ac (ts)	C_1	320.53368 (1)	321.47977	321.52674	322.39853	322.50137	--	50.4
3Aa (ts)	C_1	320.53372 (1)	321.47926	321.52630	322.39839	322.50109	--	50.3

[a] Values in parentheses are the number of imaginary frequencies.

[b] Using MP2/6-31G* geometries.

[c] Using B3LYP/6-31G* geometries.

[d] Zero Point Vibrational Energies at HF/6-31G*, scaled by 0.8929.

Table 4s. Summary of the MP2(full)/6-31G* Bond Critical Point Data for the Hydrogen Bonds of Nitroethylenes **1Aa** and **2Aa** and Their *aci*Nitro Tautomers, **1Ba** and **2Ba**.[a]

Compound	ε	ρ(r)	$\nabla^2\rho(r)$	H(r)
1Aa	0.004	0.263	3.386	-0.008
2Aa	0.081	0.184	2.306	-0.003
1Ba	0.685	2.033	8.916	-3.126
2Ba	0.498	2.077	-4.582	-3.374

[a] ρ(r) is in $e.A^{-3}$; $\nabla^2\rho(r)$ is in $e.A^{-5}$; H(r) is in Hartree A^{-3}.

Table 5s. NPA group charges of R-C^1(H)=C^2(H)-NO_2 at MP2(full)/6-31G*.

Compound	R	Group Charges			
		R	C^1H	C^2H	NO_2
Nitroethylene	H	0.25	-0.15	0.14	-0.25
Cis-1-nitropropene, **3Aa**	CH_3	0.06	0.09	0.14	-0.28
Cis 2-nitrovinylamine, **2Aa**	NH_2	0.07	0.27	0.01	-0.35
Cis-2-nitrovinylalcohol, **1Aa**	OH	-0.14	0.44	0.0	-0.30