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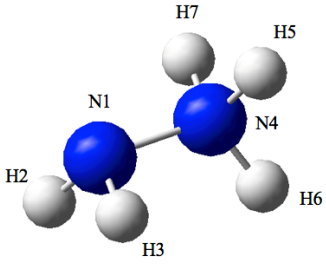
Force Field for the Atomistic Simulation of the Properties of Hydrazine, Organic Hydrazine Derivatives, and Energetic Hydrazinium Ionic Liquids

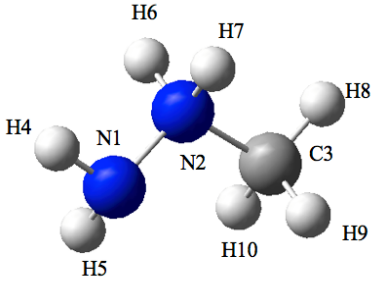
Keith E. Gutowski, Burcu Gurkan, and Edward J. Maginn

HYDRAZINIUM AND NITRATE FORCE FIELDS

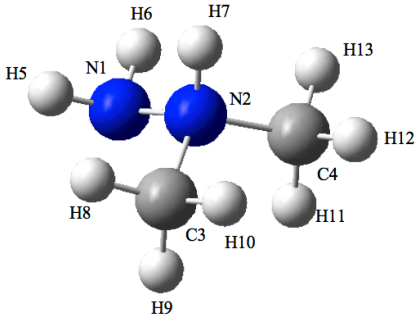
Figure S1. Structures of $N_2H_5^+$, MMH^+, $UDMH^+$, MEH^+, 2-HEH^+, and NO_3^- (optimized at B3LP/TZVP level) and corresponding atom labels.



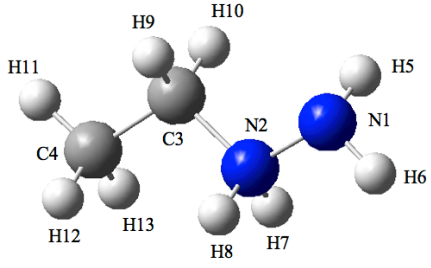
$N_2H_5^+$



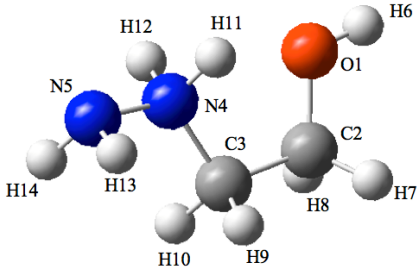
MMH^+ ($CH_3N_2H_4^+$)

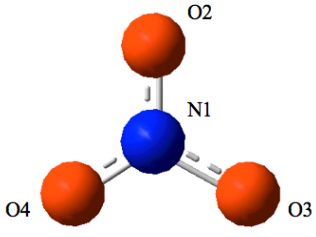


$UDMH^+$ ($(CH_3)_2N_2H_3^+$)



MEH^+ ($C_2H_5N_2H_4^+$)





2-HEH$^+$ **NO_3^-**

Table S1. Partial atomic charges (CHELPG at B3LYP/TZVP level) and atom types for $N_2H_5^+$, MMH^+, $UDMH^+$, MEH^+, 2-HEH^+, and NO_3^-.

$N_2H_5^+$				**MMH^+**				**$UDMH^+$**		
Atom	**Type**	**q_i (e)**		**Atom**	**Type**	**q_i (e)**		**Atom**	**Type**	**q_i (e)**
N1	NH2	-0.7142		N1	NH2	-0.7641		N1	NH2	-0.7037
H2	HT	0.4190		N2	NH3	-0.0204		N2	NH3	0.0831
H3	HT	0.4190		C3	CT3	-0.2320		C3	CT3	-0.2342
N4	NH3	-0.0784		H4	HT	0.4245		C4	CT3	-0.2342
H5	HT	0.3182		H5	HT	0.4245		H5	HT	0.3926
H6	HT	0.3182		H6	HT	0.3460		H6	HT	0.3926
H7	HT	0.3182		H7	HT	0.3460		H7	HT	0.2970
				H8	HA3	0.1585		H8	HA3	0.1678
				H9	HA3	0.1585		H9	HA3	0.1678
				H10	HA3	0.1585		H10	HA3	0.1678
								H11	HA3	0.1678
								H12	HA3	0.1678
								H13	HA3	0.1678
MEH^+				**2-HEH^+**				**NO_3^-**		
Atom	**Type**	**q_i (e)**		**Atom**	**Type**	**q_i (e)**		**Atom**	**Type**	**q_i (e)**
N1	NH2	-0.7589		O1	OH1	-0.6677		N1	NO3	1.0721
N2	NH3	-0.0083		C2	CT2	0.2019		O2	O3N	-0.6907
C3	CT2	0.0515		C3	CT2	-0.1283		O3	O3N	-0.6907
C4	CT3	-0.2625		N4	NH3	0.1533		O4	O3N	-0.6907
H5	HT	0.4112		N5	NH2	-0.8030				
H6	HT	0.4112		H6	HO1	0.4636				
H7	HT	0.3250		H7	HA2	0.0605				
H8	HT	0.3250		H8	HA2	0.0605				
H9	HA2	0.0837		H9	HA2	0.1175				
H10	HA2	0.0837		H10	HA2	0.1175				
H11	HA3	0.1128		H11	HT	0.2943				
H12	HA3	0.1128		H12	HT	0.2943				
H13	HA3	0.1128		H13	HT	0.4178				
				H14	HT	0.4178				

Table S2. Lennard-Jones parameters and associated atoms types for $N_2H_5^+$, MMH^+, $UDMH^+$, MEH^+, 2-HEH^+, and NO_3^-.

Type	**σ (Å)**	**ε_i (kJ mol^{-1})**
NH2	3.368	0.71128
NH3	3.368	0.71128
HT	1.559	0.06569
CT2	4.009	0.33472
CT3	4.009	0.33472
HA2	2.388	0.11715
HA3	2.388	0.11715
OH1	3.029	0.63639
HO1	0.400	0.19246
NO3	3.059	0.33765
O3N	2.771	0.60961

Table S3. Bond, angle, and dihedral force field parameters for $N_2H_5^+$.

Bonds	**Force Constant k_b (kJ mol^{-1} Å^{-2})**	**r_0 (Å)**		**Angles**	**Force Constant k_θ (kJ mol^{-1} rad^{-2})**	**θ_0 (deg)**
NH2-HT	1899.536	1.019		HT-NH2-NH3	271.96	108.08
NH3-HT	1761.464	1.028		HT-NH2-HT	188.28	109.12
NH2-NH3	1355.616	1.452		HT-NH3-NH2	209.20	110.96
				HT-NH3-HT	188.28	107.84

Dihedrals	**Force Constant k_χ (kJ mol^{-1})**	**n**	**δ**
HT-NH2-NH3-HT	0.65480	3	0.0

Table S4. Bond, angle, and dihedral force field parameters for MMH^+.

Bonds	Force Constant k_b (kJ mol^{-1} Å^{-2})	r_0 (Å)	Angles	Force Constant k_θ (kJ mol^{-1} rad^{-2})	θ_0 (deg)
CT3-NH3	1179.888	1.508	HT-NH2-NH3	271.96	108.2
NH3-NH2	1397.456	1.451	HT-NH2-HT	188.28	108.87
NH2-HT	1899.536	1.019	HT-NH3-NH2	209.20	110.08
NH3-HT	1761.464	1.027	HT-NH3-HT	188.28	107.11
CT3-HA3	1456.032	1.088	HT-NH3-CT3	188.28	109.08
			HA3-CT3-NH3	230.12	108.03
			HA3-CT3-HA3	146.44	110.87
			CT3-NH3-NH2	313.80	111.17

Dihedrals	Force Constant k_χ (kJ mol^{-1})	n	δ
HA3-CT3-NH3-HT	0.52467	3	0.0
HA3-CT3-NH3-NH2	0.73973	1	0.0
HT-NH2-NH3-HT	0.65480	3	0.0
HT-NH2-NH3-CT3	-1.06441	1	0.0
HT-NH2-NH3-CT3	-0.63471	2	180.0
HT-NH2-NH3-CT3	0.48325	3	0.0
HT-NH2-NH3-CT3	-0.41547	4	180.0

Table S4. Bond, angle, and dihedral force field parameters for $UDMH^+$.

Bonds	**Force Constant k_b (kJ mol^{-1} Å^{-2})**	**r_0 (Å)**		**Angles**	**Force Constant k_θ (kJ mol^{-1} rad^{-2})**	**θ_0 (deg)**
CT3-NH3	1179.888	1.505		HT-NH2-NH3	271.96	108.33
NH3-NH2	1397.456	1.452		HT-NH2-HT	188.28	108.69
NH2-HT	1899.536	1.019		HT-NH3-NH2	209.20	111.52
NH3-HT	1761.464	1.027		HT-NH3-CT3	188.28	107.78
CT3-HA3	1456.032	1.088		HA3-CT3-NH3	230.12	108.28
				HA3-CT3-HA3	146.44	110.63
				CT3-NH3-NH2	313.80	108.91
				CT3-NH3-CT3	292.88	111.97

Dihedrals	**Force Constant k_χ (kJ mol^{-1})**	**n**	**δ**
HA3-CT3-NH3-HT	0.52467	3	0.0
HA3-CT3-NH3-NH2	0.73973	1	0.0
HA3-CT3-NH3-CT3	0.43263	3	0.0
HT-NH2-NH3-HT	0.65480	3	0.0
HT-NH2-NH3-CT3	-1.06441	1	0.0
HT-NH2-NH3-CT3	-0.63471	2	180.0
HT-NH2-NH3-CT3	0.48325	3	0.0
HT-NH2-NH3-CT3	-0.41547	4	180.0

Table S4. Bond, angle, and dihedral force field parameters for MEH^+.

Bonds	Force Constant k_b (kJ mol^{-1} Å^{-2})	r_0 (Å)	Angles	Force Constant k_θ (kJ mol^{-1} rad^{-2})	θ_0 (deg)
NH2-HT	1903.720	1.019	HT-NH2-NH3	271.96	108.03
NH2-NH3	1410.008	1.448	HT-NH2-HT	188.28	108.52
NH3-HT	1778.200	1.026	HT-NH3-NH2	209.20	106.38
NH3-CT2	983.240	1.527	HT-NH3-HT	188.28	104.86
CT2-HA2	1443.480	1.090	HT-NH3-CT2	188.28	109.61
CT2-CT3	1255.200	1.518	HA2-CT2-NH3	230.12	105.83
CT3-HA3	1443.480	1.092	HA2-CT2-HA2	146.44	108.96
			CT2-NH3-NH2	313.80	119.06
			HA2-CT2-CT3	188.28	112.58
			HA3-CT3-CT2	188.28	109.93
			HA3-CT3-HA3	146.44	107.94
			CT3-CT2-NH3	292.88	110.64

Dihedrals	Force Constant k_χ (kJ mol^{-1})	n	δ
HT-NH2-NH3-HT	0.65480	3	0.0
HT-NH2-NH3-CT2	-1.06441	1	0.0
HT-NH2-NH3-CT2	-0.63471	2	180.0
HT-NH2-NH3-CT2	0.48325	3	0.0
HT-NH2-NH3-CT2	-0.41547	4	180.0
HT-NH3-CT2-CT3	0.56024	3	0.0
HT-NH3-CT2-HA2	0.52467	3	0.0
NH2-NH3-CT2-CT3	10.28804	1	0.0

NH2-NH3-CT2-HA2	0.73973	3	0.0
HA3-CT3-CT2-NH3	0.56610	3	0.0
HA3-CT3-CT2-HA2	0.60333	3	0.0

Table S5. Bond, angle, and dihedral force field parameters for 2-HEH$^+$.

Bonds	Force Constant k_b (kJ mol^{-1} Å^{-2})	r_0 (Å)		Angles	Force Constant k_θ (kJ mol^{-1} rad^{-2})	θ_0 (deg)
NH2-HT	1899.536	1.018		HT-NH2-NH3	271.96	108.22
NH2-NH3	1397.456	1.444		HT-NH2-HT	188.28	108.79
NH3-HT	1761.464	1.028		HT-NH3-NH2	209.20	107.44
NH3-CT2	1037.632	1.519		HT-NH3-HT	188.28	105.33
CT2-HA2	1456.032	1.092		HT-NH3-CT2	188.28	108.23
CT2-CT2	1271.936	1.523		HA2-CT2-NH3	230.12	107.32
CT2-OH1	1497.872	1.428		HA2-CT2-HA2	146.44	109.27
OH1-HO1	2196.600	0.966		CT2-NH3-NH2	313.80	119.34
				HA2-CT2-CT2	188.28	111.02
				CT2-CT2-NH3	292.88	107.73
				HA2-CT2-OH1	251.04	111.95
				HO1-OH1-CT2	217.57	111.48
				OH1-CT2-CT2	334.72	104.45

Dihedrals	Force Constant k_χ (kJ mol^{-1})	n	δ
HT-NH2-NH3-HT	0.65480	3	0.0
HT-NH2-NH3-CT2	-1.06441	1	0.0
HT-NH2-NH3-CT2	-0.63471	2	180.0
HT-NH2-NH3-CT2	0.48325	3	0.0
HT-NH2-NH3-CT2	-0.41547	4	180.0
HT-NH3-CT2-CT2	0.56024	3	0.0
HT-NH3-CT2-HA2	0.52467	3	0.0

NH2-NH3-CT2-CT2	10.28804	1	0.0
NH2-NH3-CT2-HA2	0.73973	3	0.0
NH3-CT2-CT2-HA2	0.56610	3	0.0
NH3-CT2-CT2-OH1	4.00200	1	0.0
NH3-CT2-CT2-OH1	-0.62886	2	180.0
NH3-CT2-CT2-OH1	-0.82634	3	0.0
NH3-CT2-CT2-OH1	-1.63469	4	180.0
NH3-CT2-CT2-OH1	0.60375	5	0.0
HA2-CT2-CT2-HA	0.60333	3	0.0
HA2-CT2-CT2-OH1	0.80919	3	0.0
HO1-OH1-CT2-CT2	-2.70956	1	0.0
HO1-OH1-CT2-CT2	0.18577	2	180.0
HO1-OH1-CT2-CT2	0.91086	3	0.0
HO1-OH1-CT2-HA2	0.73973	3	0.0

Table S6. Bond, angle, and improper force field parameters for NO_3^-.

Bonds	**Force Constant** k_b **(kJ mol^{-1} Å^{-2})**	r_0 **(Å)**		**Angles**	**Force Constant** k_θ **(kJ mol^{-1} rad^{-2})**	θ_0 **(deg)**
NO3-O3N	2196.60	1.2676		O3N-NO3-O3N	439.32	120.0

Impropers	**Force Constant** k_ψ **(kJ mol^{-1} rad^{-2})**	ψ_0
NO3-O3N-O3N-O3N	251.04	0.0