Supplementary Materials: **Thermochemistry, Bond Energies and Internal Rotor Potentials of Acetic Acid Hydrazide, Acetamide, *N*-Methyl Acetamide (NMA) and Radicals**

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SM-0. Geometric Parameters of the parent molecules optimized at the B3LYP/6-31G(d,p) level.

Table S1. $CH_3CONHNH_2$:

Definition [b]	Bond (Å)	Angle[c]	Value (°)	Dihedral Angle [d]	Value (°)
R(1,2)	1.0954	A(2,1,3)	109.1787	D(2,1,5,6)	−120.0362
R(1,3)	1.0893	A(2,1,4)	107.4742	D(2,1,5,7)	59.9657
R(1,4)	1.0954	A(2,1,5)	111.5778	D(3,1,5,6)	−0.1366
R(1,5)	1.5204	A(3,1,4)	109.1662	D(3,1,5,7)	179.8653
R(5,6)	1.2223	A(3,1,5)	107.8488	D(4,1,5,6)	119.7359
R(5,7)	1.3748	A(4,1,5)	111.558	D(4,1,5,7)	−60.2622
R(7,8)	1.0111	A(1,5,6)	123.161	D(1,5,7,8)	179.95
R(7,9)	1.4018	A(1,5,7)	116.1035	D(1,5,7,9)	0.0709
R(9,10)	1.0172	A(6,5,7)	120.7354	D(6,5,7,8)	−0.0482
R(9,11)	1.0172	A(5,7,8)	116.3213	D(6,5,7,9	−179.9273
		A(5,7,9)	127.8178	D(5,7,9,10)	−60.2445
		A(8,7,9)	115.8608	D(5,7,9,11)	60.0643
		A(7,9,10)	110.5502	D(8,7,9,10)	119.8759
		A(7,9,11)	110.5555	D(8,7,9,11)	−119.8153
		A(10,9,11)	108.6151		

Table S2. CH_3CONH_2:.

Definition [b]	Bond(Å)	Angle [c]	Value (°)	Dihedral Angle [d]	Value (°)
R(1,2)	1.0933	A(2,1,3)	109.1337	D(2,1,5,6)	175.5263
R(1,3)	1.0926	A(2,1,4)	108.9088	D(2,1,5,7)	−4.7606
R(1,4)	1.0936	A(2,1,5)	114.0424	D(3,1,5,6)	53.6333
R(1,5)	1.5225	A(3,1,4)	107.3428	D(3,1,5,7)	−126.6535
R(5,6)	1.2215	A(3,1,5)	108.5547	D(4,1,5,6)	−62.7996
R(5,7)	1.3677	A(4,1,5)	108.6505	D(4,1,5,7)	116.9136
R(7,8)	1.006	A(1,5,6)	122.2217	D(1,5,7,8)	−0.456
R(7,9)	1.0086	A(1,5,7)	115.5143	D(1,5,7,9)	−178.977
		A(6,5,7)	122.2633	D(6,5,7,8)	179.257
		A(5,7,8)	122.9393	D(6,5,7,9)	0.7361
		A(5,7,9)	117.9815		
		A(8,7,9)	119.063		

Table S3. $CH_3CONHCH_3$:.

Definition [b]	Bond (Å)	Angle [c]	Value (°)	Dihedral Angle [d]	Value (°)
R(1,2)	1.0893	A(2,1,3)	109.1329	D(2,1,5,6)	−1.7928
R(1,3)	1.0955	A(2,1,4)	109.3386	D(2,1,5,7)	179.2534
R(1,4)	1.0952	A(2,1,5)	107.9436	D(3,1,5,6)	117.9211
R(1,5)	1.5209	A(3,1,4)	107.5181	D(3,1,5,7)	−61.0328
R(5,6)	1.2242	A(3,1,5)	111.2595	D(4,1,5,6)	−121.9736
R(5,7)	1.3725	A(4,1,5)	111.6162	D(4,1,5,7)	59.0725
R(7,8)	1.0109	A(1,5,6)	122.4507	D(1,5,7,8)	−175.8633
R(7,9)	1.4516	A(1,5,7)	116.4536	D(1,5,7,9)	−8.9124
R(9,10)	1.0924	A(6,5,7)	121.0873	D(6,5,7,8)	5.1676
R(9,11)	1.0991	A(5,7,8)	113.1617	D(6,5,7,9)	172.1185
R(9,12)	1.0935	A(5,7,9)	127.2302	D(5,7,9,10)	166.5334
		A(8,7,9)	118.3699	D(5,7,9,11)	−73.4016
		A(7,9,10)	108.8639	D(5,7,9,12)	48.4813
		A(7,9,11)	113.175	D(8,7,9,10)	−27.1126
		A(7,9,12)	111.022	D(8,7,9,11)	92.9525
		A(10,9,11)	107.9737	D(8,7,9,12)	−145.1646
		A(10,9,12)	107.4223		
		A(11,9,12)	108.1842		

Geometry optimized at the B3LYP/6-31G(d,p) density functional calculation level. [b] Bond length or the distance between the two atoms of a given number. [c] Bond angle or the angle among the three atoms of a given number. [d] Dihedral angle among the four atoms of a given number.

SM-1. Moments of Inertia and Vibrational Frequencies of parent molecules and radicals:

Table S4. Moments of Inertia (amu bohr [2]) [a].

Species	I [a]	I [b]	I [c]
CH3CONHNH2	203.33749	431.26258	613.54529
C•H2–C=ONHNH2	181.75858	430.35230	601.04696
CH3–C=ON•NH2	166.80977	422.28714	577.91961

CH3–C=ONHN•H	198.87470	399.58078	587.37889
CH3CONH2	167.33149	195.80982	351.97451
C•H2–C=ONH2	161.38272	176.80045	337.65175
CH3–C=ON•H	149.54610	197.76796	334.86688
CH3CONHCH3	206.50339	442.22339	625.31905
C•H2–C=ONHCH3	183.97873	441.11007	613.69261
CH3–C=ON•CH3	179.32554	454.15378	599.01790
CH3–C=ONHC•H2	201.80783	413.50651	604.04129

[a] Optimized at the B3LYP/6-31G(d,p) level of theory.

Table S5. Vibration Frequencies (cm^{-1}) [a].

$CH_3CONHNH_2$	115.1	284.8	289.5	497.0	564.8	582.7	596.4	792.7	893.1	1014.3
	1051.2	1218.2	1320.7	1359.3	1410.5	1446.6	1479.8	1499.1	1695.3	1800.5
	3050.4	3111.4	3178.5	3471.1	3562.4	3618.4				
$C•H_2–C=ONHNH_2$	63.5	268.9	303.0	318.9	476.4	551.0	582.8	594.4	735.4	820.3
	923.9	992.3	1222.3	1317.0	1366.0	1432.5	1473.5	1671.9	1694.2	3183.3
	3302.2	3468.5	3562.4	3618.5						
$CH_3–C=ON•NH_2$	118.0	231.9	332.0	443.6	539.3	647.1	678.1	857.7	1020.7	1052.4
	1239.4	1268.5	1395.1	1411.5	1490.6	1491.6	1570.3	1694.8	3058.9	3123.1
	3165.2	3445.1	3711.4							
$CH_3–C=ONHN•H$	198.9	291.9	435.6	494.3	598.3	601.4	681.8	818.5	1007.4	1055.2
	1240.3	1285.7	1368.8	1414.8	1473.8	1482.6	1551.9	1794.0	3069.4	3134.2
	3182.6	3427.8	3505.0							
CH_3CONH_2	113.1	429.8	522.0	540.4	674.9	842.6	988.0	1058.8	1123.4	1351.9
	1412.7	1486.8	1505.1	1626.8	1810.7	3061.0	3138.6	3146.5	3609.0	3751.9
$C•H_2–C=ONH_2$	265.5	309.6	418.1	498.9	547.3	600.1	734.6	917.4	955.5	1119.4
	1353.3	1480.1	1619.5	1702.9	3168.7	3294.7	3597.5	3731.8		
$CH_3–C=ON•H$	397.8	463.4	507.7	577.0	833.0	947.3	1030.6	1123.0	1309.4	1406.1
	1477.2	1485.3	1589.6	3060.8	3128.3	3169.4	3443.7	3103.9		
	3145.0	3440.6								
$CH_3CONHCH_3$	146.0	282.0	475.7	515.8	573.3	625.4	805.4	992.7	1053.6	1095.0
	1149.3	1200.2	1349.5	1410.7	1467.8	1475.4	1492.1	1500.1	1508.1	1534.4
	1797.9	3015.7	3050.7	3095.5	3113.0	3136.4	3177.6	3624.9		
$C•H_2–C=ONHCH_3$	126.3	278.7	285.1	448.5	476.4	564.4	594.7	735.2	858.1	991.7
	1103.1	1155.9	1207.0	1359.2	1447.2	1477.9	1492.0	1502.2	1535.8	1677.5
	3022.2	3072.2	3139.3	3182.1	3300.5	3646.7				
$CH_3–C=ON•CH_3$	136.3	285.6	402.7	526.1	615.1	783.9	974.3	1034.0	1043.4	1103.4
	1141.1	1285.7	1402.3	1415.9	1460.8	1478.8	1486.1	1500.0	1651.0	3003.5
	3057.7	3060.7	3110.5	3123.7	3167.9					
$CH_3–C=ONHC•H_2$	89.9	207.1	284.8	293.6	481.6	545.6	580.6	717.1	806.5	983.2
	1049.7	1108.6	1253.3	1343.0	1409.5	1467.0	1486.6	1495.4	1524.1	1778.3
	3047.5	3108.5	3178.2	3224.3	3350.4	3597.9				

[a]Frequencies calculated at the B3LYP/6-31G(d,p) level of theory.

SM-2. Mulliken Atomic Charges

Table S6. (I) Mulliken Atomic Charges for Acetohydrazide and its Radicals.

$CH_3CONHNH_2$		$C•H_2CONHNH_2$		$CH_3CON•NH_2$		$CH_3CONHN•H$	
Atoms	**Charges**	**Atoms**	**Charges**	**Atoms**	**Charges**	**Atoms**	**Charges**
1 C	−0.402315	1 C	−0.234273	1 C	−0.377199	1 C	−0.375741
2 H	0.121192	2 H	0.143004	2 H	0.128190	2 H	0.147242
3 H	0.150336	3 H	0.099884	3 H	0.137384	3 H	0.136885
4 H	0.121365	4 C	0.570321	4 H	0.138721	4 H	0.147356
5 C	0.558623	5 O	−0.504403	5 C	0.510877	5 C	0.553199
6 O	−0.494651	6 N	−0.423541	6 O	−0.490789	6 O	−0.469507
7 N	−0.406385	7 H	0.278899	7 N	−0.300686	7 N	−0.340122
8 H	0.277625	8 N	−0.456181	8 N	−0.335637	8 H	0.271718
9 N	−0.451870	9 H	0.265755	9 H	0.292639	9 N	−0.317619
10 H	0.263059	10 H	0.260536	10 H	0.296499	10 H	0.246589
11 H	0.263020						

Table S7. (II) Mulliken Atomic Charges for Acetamide and its Radicals.

CH_3CONH_2		$C•H_2CONH_2$		$CH_3CON•H$	
Atoms	**Charges**	**Atoms**	**Charges**	**Atoms**	**Charges**
1 C	−0.055334	1 C	−0.067481	1 C	−0.046469
2 H	−0.022534	2 H	0.018583	2 H	0.036769
3 H	0.019714	3 H	0.049910	3 H	0.025065
4 H	0.016401	4 C	0.914210	4 H	0.022283
5 C	1.077024	5 O	−0.665853	5 C	0.555443
6 O	−0.764450	6 N	−0.671122	6 O	−0.461093
7 N	−0.696651	7 H	0.208977	7 N	−0.342651
8 H	0.211890	8 H	0.212777	8 H	0.210653
9 H	0.213941				

Table S8. (III) Mulliken Atomic Charges for *N*-Methyl Acetamide and its Radicals.

$CH_3CONHCH_3$		$C•H_2CONHCH_3$		$CH_3CON•CH_3$		$CH_3CONHC•H_2$	
Atoms	**Charges**	**Atoms**	**Charges**	**Atoms**	**Charges**	**Atoms**	**Charges**
1 C	−0.360700	1 C	−0.234608	1 C	−0.067856	1 C	−0.401136
2 H	0.142160	2 H	0.137113	2 H	0.015848	2 H	0.146128
3 H	0.138604	3 H	0.110454	3 H	0.016119	3 H	0.132117
4 H	0.137617	4 C	0.562523	4 H	0.024339	4 H	0.131456
5 C	0.463021	5 N	−0.525521	5 C	0.802512	5 C	0.535968
6 O	−0.426924	6 H	0.268023	6 O	−0.573036	6 O	−0.488515
7 N	−0.531373	7 C	−0.171936	7 N	−0.443796	7 N	−0.442833
8 H	0.260401	8 H	0.122700	8 C	0.180754	8 H	0.277077
9 C	−0.180559	9 H	0.122862	9 H	0.014106	9 C	−0.129519
10 H	0.114890	10 H	0.122867	10 H	0.029614	10 H	0.116521
11 H	0.122017	11 O	−0.514477	11 H	0.001397	11 H	0.122736
12 H	0.120846						