Table S-1. Total Energies (hartree) and Zero-Point Vibrational Energies (kcal mol^{-1}) of the Transition States for the Rotation and Inversion in Nitrosoheterocycles 1-4 derived with the B3LYP method.[a]

species	basis set			
	6-31+G*		6-311+G**	
	E_T	ZPVE	E_T	ZPVE
TS_{inv}-1 (C_s)	-263.21303	41.57	-263.27863	41.26
sp-**TS_{rot}-1** (C_s)	-263.20741	41.08	-263.27327	40.80
ap-**TS_{rot}-1** (C_s)	-263.21367	41.30	-263.27987	41.01
sp-**TS_{rot}-2** (C_s)	-340.62809	63.07	-340.71211	62.68
ap-**TS_{rot}-2** (C_s)	-340.63626	63.13	-340.72049	62.75
TS_{inv}-3 (C_s)	-416.81325	70.94	-416.91137	70.60
sp-**TS_{rot}-3** (C_s)	-416.76862	69.66	-416.86765	69.35
ap-**TS_{rot}-3** (C_s)	-416.78317	70.09	-416.88210	69.79
TS_{inv}-4				
sp-**TS_{rot}-4** (C_s)	-378.66179	66.39	-378.75174	66.00
ap-**TS_{rot}-4** (C_s)	-378.67604	66.79	-378.76591	66.41

[a]See Figure S-1,2,3,4 for B3LYP structures of the transition states.

Table S-2. Total Energies (hartree) and Zero-Point Vibrational Energies (kcal mol^{-1}) of the Initial Compound, Products, and Transition States for the Cheletropic Fragmentation of 1-Nitrosoaziridine (1).

level	1	*sp*-TS_{lin}-1	*ap*-TS_{lin}-1	TS_{nonlin}-1	CH_2=CH_2	N_2O
B3LYP/A[a]						
E_T	-263.22276	-263.18593	-263.15074	-263.14004	-78.59327	-184.66830
ZPVE	41.91	39.63	38.80	38.97	32.06	6.94
B3LYP/B[a]						
E_T	-263.28839	-263.25245	-263.21775	-263.20760	-78.61551	-184.71823
ZPVE	41.60	39.39	38.51	38.67	31.87	6.91
B3LYP/C[a]						
E_T	-263.30821	-263.27219	-263.23690	-263.22644	-78.62208	-184.73335
ZPVE	41.68	39.42	38.60	38.69	31.95	7.02
MP2/A						
E_T	-262.45512	-262.41019	-262.36519	-262.38205	-78.29118	-184.21442
ZPVE	42.45	40.05	39.39	42.87	32.50	6.57
MP2/B						
E_T	-262.58335	-262.53672	-262.49170	-262.51480	-78.34630	-184.29003
ZPVE	42.21	39.80	39.10	42.81	32.09	6.58
CCD/A						
E_T	-262.46851	-262.41383	-262.37546	-262.34607	-78.31545	-184.18918
CCSD(T)/A// CCD/A						
E_T	-262.51093	-262.47141	-262.43199	-262.43540	-78.32787	-184.22207

[a]Basis set "A" is 6-31+G(d), "B" is 6-311+G(d,p), and "C" is 6-311++G(3df,2pd).

Table S-3. Total Energies (hartree) and Zero-Point Vibrational Energies (kcal mol^{-1}) of the Initial Compound, Products[a], and Transition State for the Cheletropic Fragmentation of 1-Nitroso-Δ^3-pyrroline (2).

level	**2**	**TS-2**	**SP-2**[b]	*cis*-butadiene
B3LYP/6-31+G*				
E_T	-340.67699	-340.57901	-340.55305	-155.99536
ZPVE	64.37	61.03	60.91	53.40
B3LYP/6-311+G**				
E_T	-340.76031	-340.66460	-340.63908	-156.03519
ZPVE	63.99	60.70	60.6	53.09
MP2/6-31+G*				
E_T	-339.64924	-339.54311	-339.50964	-155.42982
ZPVE	65.15	62.22	62.12	53.99

[a]See Table S-2 for energies of nitrous oxide. [b]A second order saddle point obtained under C_s symmetry constraint.

Table S-4. Total Energies (hartree) and Zero-Point Vibrational Energies (kcal mol^{-1}) of the Initial Compounds, Products[a], and Transition States for the Cheletropic Fragmentation of 7-Nitroso-7-azabicyclo[2.2.1]hepta-2,5-diene (3) and 6-Nitroso-6-azabicyclo[2.1.1]hex-4-ene (4) derived with the B3LYP method.

species	basis set			
	6-31+G*		6-311+G**	
	E_T	ZPVE	E_T	ZPVE
3	-416.81451	71.08	-416.91259	70.75
TS-3	-416.78265	69.32	-416.88181	69.01
benzene (D_{2h})	-232.25893	63.09	-232.31124	62.82
4	-378.70413	67.70	-378.79332	67.29
TS-4	-378.68180	66.28	-378.77206	65.89
cyclopentadiene (C_{2v})	-194.11033	58.13	-194.15623	57.79

[a]See Table S-2 for energies of nitrous oxide.

Table S-5. Total Energies (hartree) and Zero-Point Vibrational Energies (kcal mol^{-1}) of *cis*-Diamines 7-9 derived with the B3LYP method.[a]

compound	basis set			
	6-31+G*		6-311+G**	
	E_T	ZPVE	E_T	ZPVE
cis-1,4-diaminobut-2-ene (**7**)	-267.92126	90.67	-268.00017	90.08
cis-1,4-diaminocyclohexa-2,5-diene (**8**)	-344.12428	98.62	-344.21730	98.12
cis-1,4-diaminocyclopent-2-ene (**9**)	-306.03299	95.02	-306.11831	94.51

[a]See Figure S-5 for B3LYP structures.

Table S-6. Selected Geometrical Parameters[a] of 1-Nitrosoaziridine (1) and Its Transition States for the Cheletropic Fragmentation.

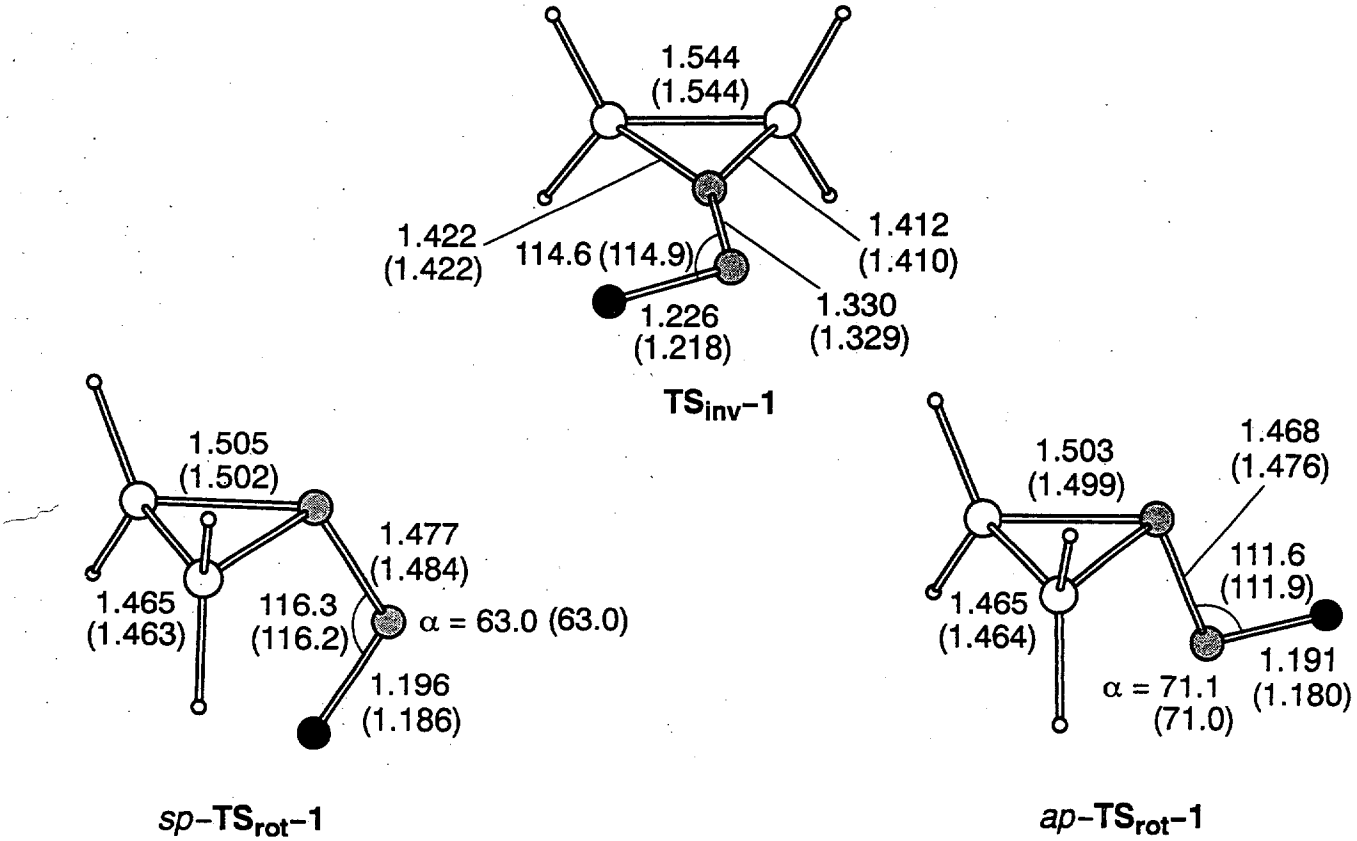
	C1-C2	C1-N1	C2-N1	N1-N2	N2-O	N1N2O	α^b
1							
B3LYP/B[c]	1.511	1.451	1.448	1.386	1.203	114.2	51.6
B3LYP/C[c]	1.506	1.446	1.444	1.383	1.200	114.3	52.0
MP2/A[c]	1.504	1.457	1.458	1.390	1.234	113.3	55.4
MP2/B	1.508	1.457	1.455	1.394	1.216	113.5	55.9
CCD/A	1.502	1.457	1.457	1.401	1.209	113.3	57.0
***sp*-TS_{lin}-1**							
B3LYP/B	1.389	1.956	1.762	1.272	1.222	127.2	68.3
B3LYP/C	1.384	1.943	1.772	1.267	1.219	127.5	68.6
MP2/A	1.385	1.919	1.919	1.255	1.247	129.0	70.3
MP2/B	1.385	1.911	1.911	1.250	1.230	129.4	70.6
CCD/A	1.377	1.941	1.941	1.247	1.233	129.0	70.7
***ap*-TS_{lin}-1**							
B3LYP/B	1.370	2.046	2.041	1.237	1.250	123.8	74.6
B3LYP/C	1.366	2.040	2.037	1.232	1.246	123.9	74.6
MP2/A	1.375	2.071	2.071	1.227	1.272	126.7	75.4
MP2/B	1.375	2.057	2.057	1.222	1.257	127.2	75.1
CCD/A	1.366	2.108	2.108	1.227	1.260	123.9	76.0
TS_{nonlin}-1							
B3LYP/B	1.434	2.451	1.547	1.227	1.218	133.6	47.8
B3LYP/C	1.430	2.446	1.543	1.222	1.214	134.0	48.4
MP2/A	1.502	2.546	1.516	1.220	1.199	154.4	46.3
MP2/B	1.505	2.549	1.511	1.217	1.185	153.8	43.6
CCD/A	1.476	2.415	1.520	1.192	1.191	150.6	47.8

[a]Bond lengths in angstroms, angles in degrees; numbering of atoms as in Figure 1.

[b]The out-of-plane angle between the N1-N2 bond and the C1N1C2 plane.

[c]Basis set "A" is 6-31+G(d), "B" is 6-311+G(d,p), and "C" is 6-311++G(3df,2pd).

Figure S-1



TS_{inv}-1

sp-TS_{rot}-1

ap-TS_{rot}-1

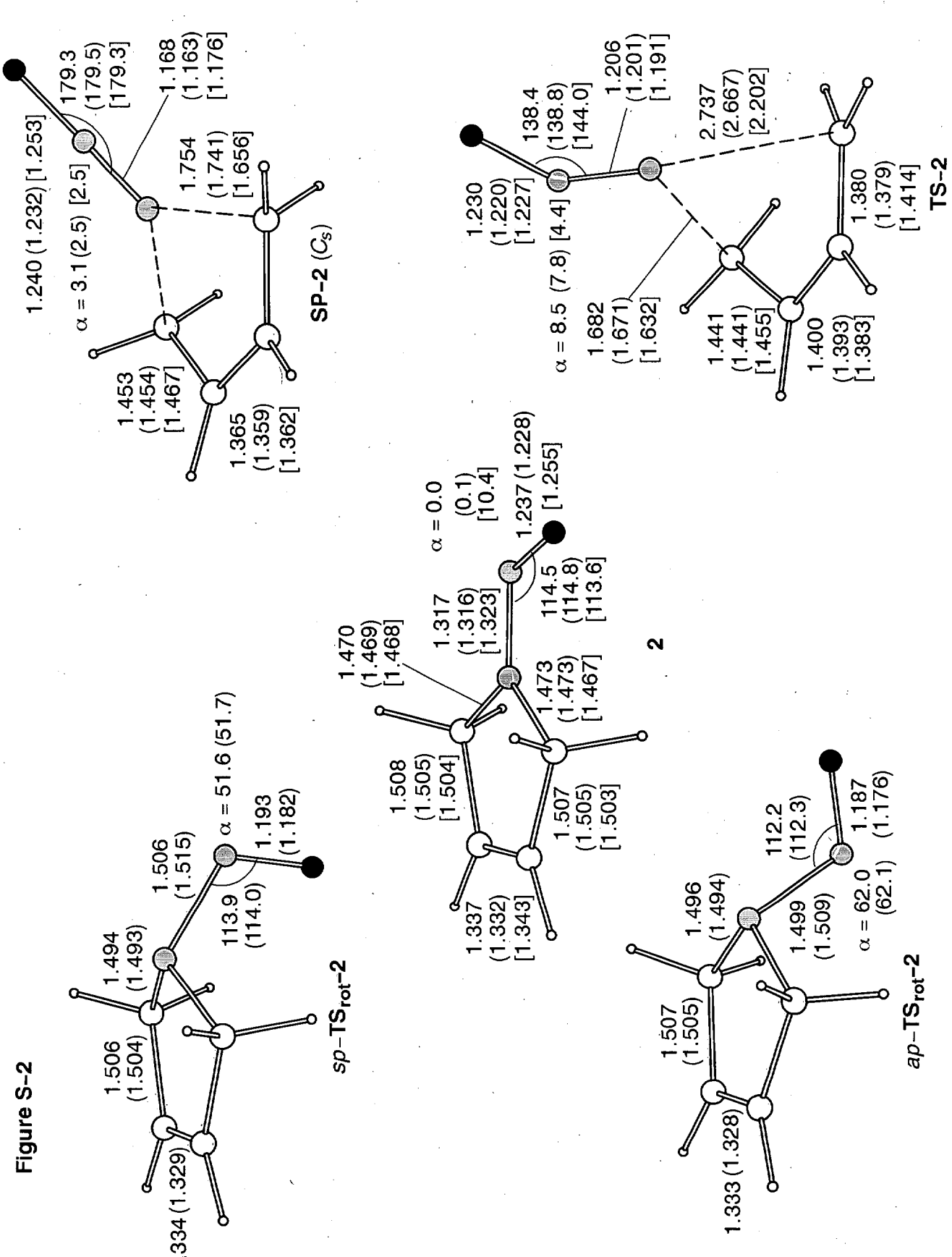
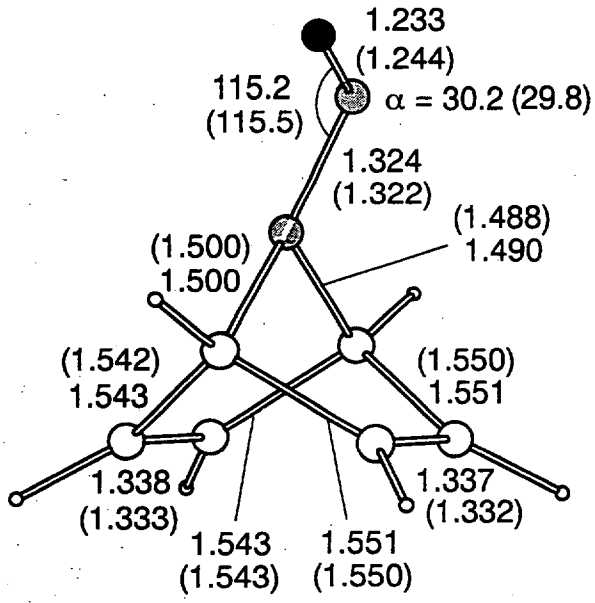


Figure S-2



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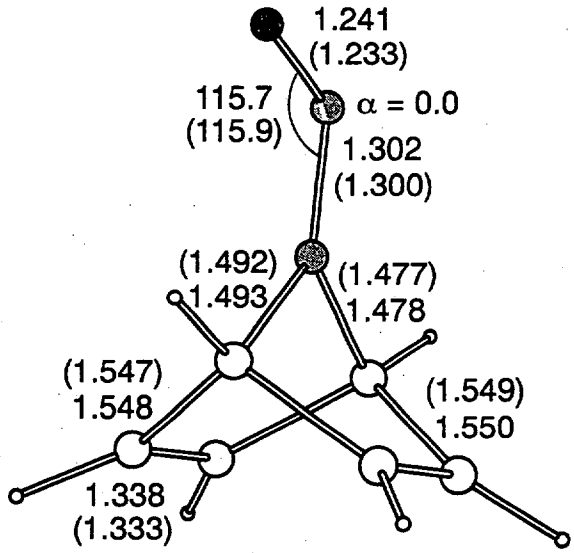

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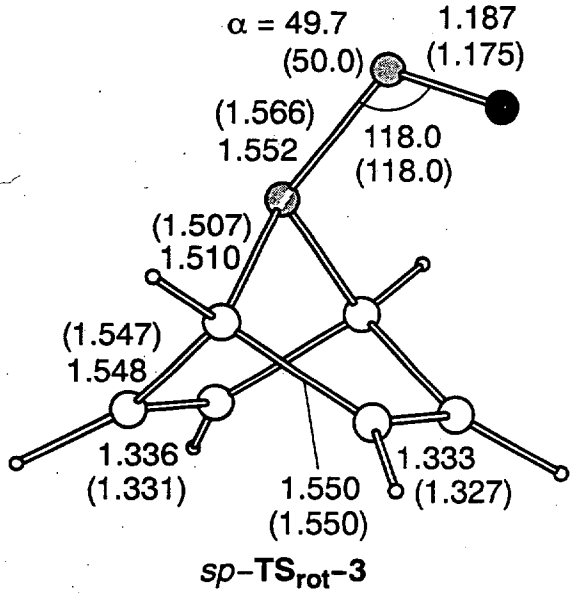

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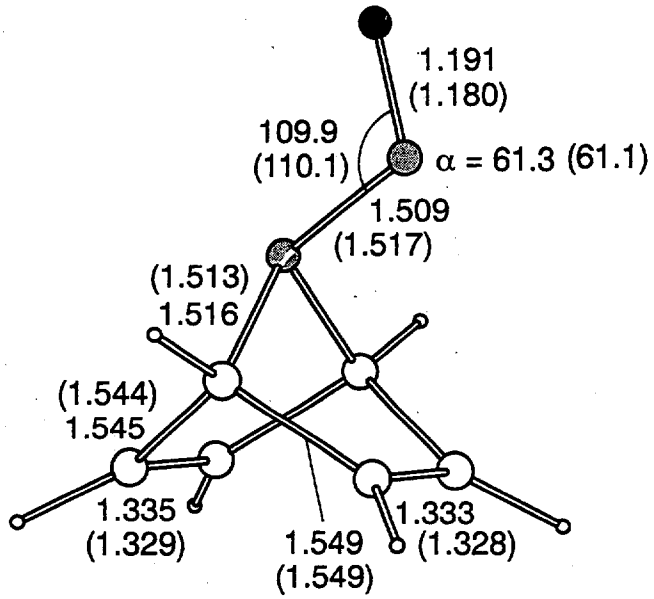

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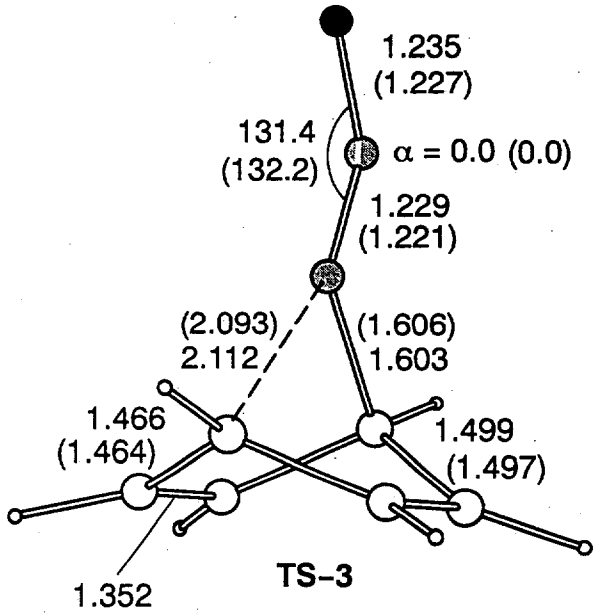
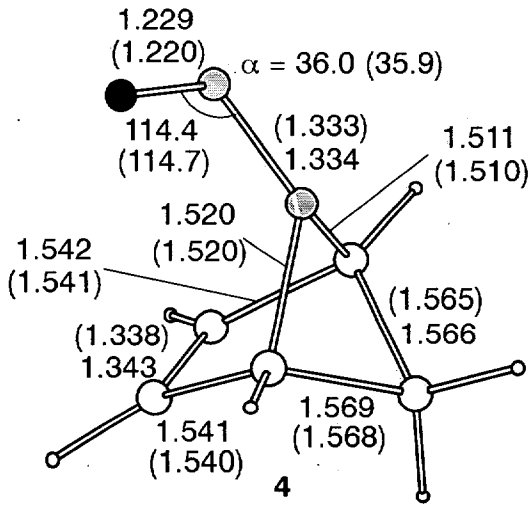


TS-3

Figure S-4



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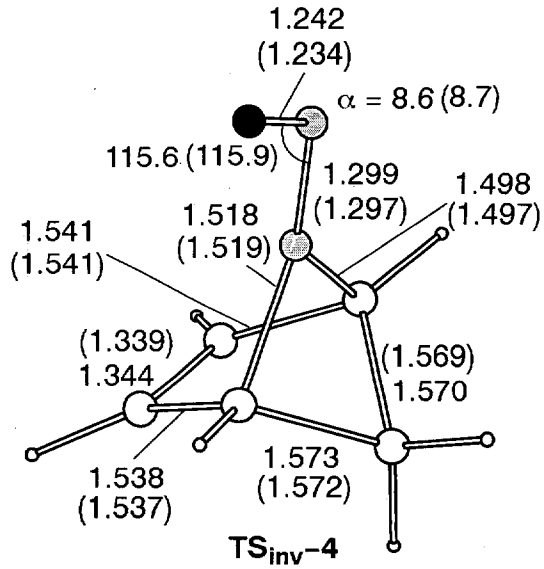
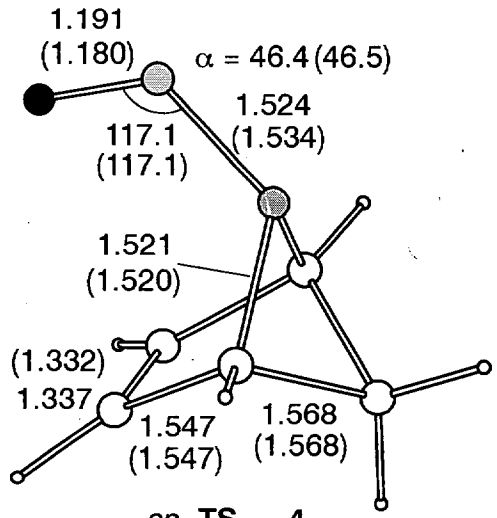
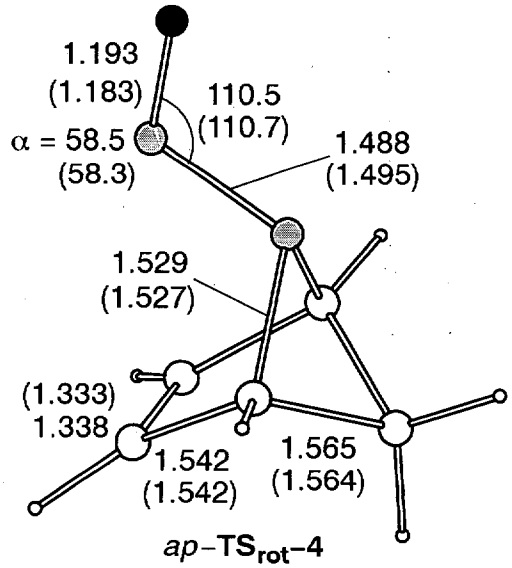


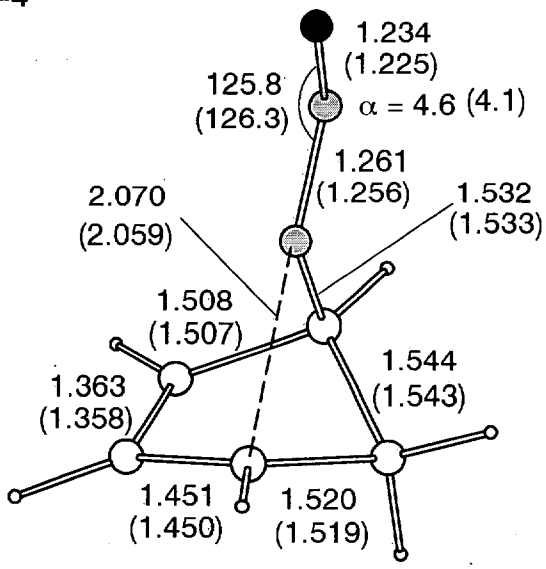
TS_{inv}-4



***sp*-TS_{rot}-4**

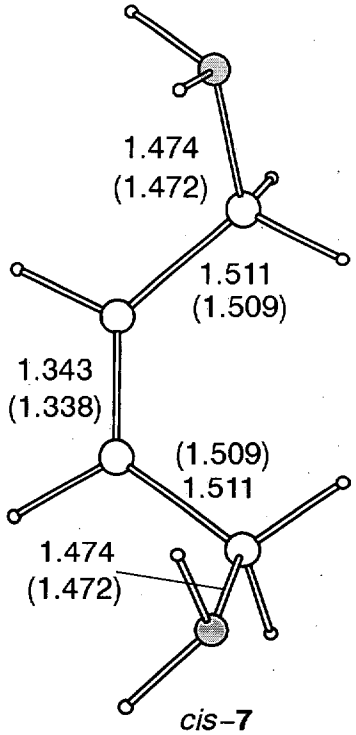


***ap*-TS_{rot}-4**

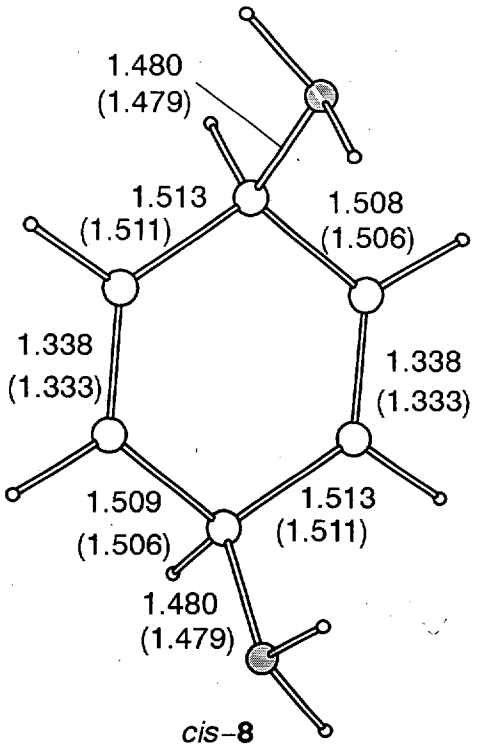


TS-4

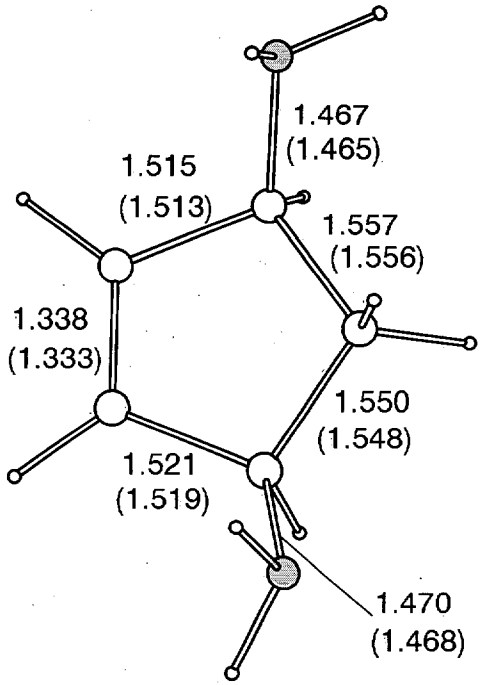
Figure S-5



cis-**7**



cis-**8**



cis-**9**

Captions to Figures

Figure S-1. B3LYP structures of the transition states for the rotations about the N-N bond and the inversion of the ring nitrogen in 1-nitrosoaziridine (**1**) calculated with the 6-31+G* and 6-311+G** (in parentheses) basis sets. The filled circles stand for oxygen and the shaded ones for nitrogen atoms.

Figure S-2. B3LYP/6-31+G*, B3LYP/6-311+G** (in parentheses) and MP2/6-31+G* structures (in square brackets) of 1-nitroso-Δ^3-pyrroline (**2**) and its transition states for the rotations, inversion, and cheletropic decomposition. The filled circles stand for oxygen and the shaded ones for nitrogen atoms.

Figure S-3. B3LYP structures of 7-nitroso-7-azabicyclo[2.2.1]hepta-2,5-diene (**3**) and its transition states for the rotations, inversion, and cheletropic decomposition calculated with the 6-31+G* and 6-311+G** (in parentheses) basis sets. The filled circles stand for oxygen and the shaded ones for nitrogen atoms.

Figure S-4. B3LYP structures of 6-nitroso-6-azabicyclo[2.1.1]hexa-4-ene (**4**) and its transition states for the rotations, inversion, and cheletropic decomposition calculated with the 6-31+G* and 6-311+G** (in parentheses) basis sets. The filled circles stand for oxygen and the shaded ones for nitrogen atoms.

Figure S-5. B3LYP structures of *cis*-diamines **7-9** calculated with the 6-31+G* and 6-311+G** (in parentheses) basis sets. The filled circles stand for oxygen and the shaded ones for nitrogen atoms.