

**Table B. B3LYP/6-31+G(d)//HF/6-31+G(d) Parameters for the Reaction of 2-Methylthiirane at C<sub>3</sub> Various Amines.**

Nucleophile	Distance <sup>a</sup> , N-C <sub>2</sub>	Distance <sup>a</sup> , C <sub>2</sub> -S	Distance <sup>a</sup> , C <sub>3</sub> -S	Angle <sup>b</sup> , NC <sub>2</sub> S	Dihedral Angles <sup>b</sup>
NH <sub>3</sub>	1.87	2.42	1.83	158	-54.6, 64.0, -175
MeNH <sub>2</sub>	1.92	2.39	1.83	160	-174, 62.5, 51.5
MeNH <sub>2</sub>	1.92	2.39	1.83	161	64.7, 89.1, -172
Me <sub>2</sub> NH	1.92	2.39	1.83	164	85.8, -44.2, -159
Me <sub>2</sub> NH	1.94	2.37	1.83	162	62.9, 171, 170
Me <sub>3</sub> N	1.93	2.39	1.84	166	-82.1, 40.8, 159

a) In Angstroms.    b) In degrees.

**Table C. MP2/6-31+G(d)//MP2/6-31+G(d) Parameters for Reactions of Thiiranes with Amines**

Reaction	N-C <sub>2</sub> <sup>a</sup>	C-F <sup>a</sup>	C <sub>2</sub> -S <sup>a</sup>	C <sub>3</sub> -S <sup>a</sup>	NC <sub>2</sub> S <sup>b</sup>	Dihedral Angles <sup>b</sup>
2-Fluorothiirane + NH <sub>3</sub> at C <sub>2</sub>	1.72	1.36	2.46	1.81	156	-59.3, -177, 60.0
2-Fluorothiirane + NH <sub>3</sub> at C <sub>3</sub>	1.88	1.43	2.35	1.75	152	-77.2, 38.2, 156
Thiirane + NH <sub>3</sub>	1.74		2.44	1.81	159	58.8, -58.8, -180
Thiirane + NH <sub>3</sub>	1.74		2.44	1.81	159	58.8, -58.8, -180
cis-2,3-Dimethylthiirane + NH <sub>3</sub>	1.84		2.44	1.82	153	-55.0, 62.2, -176
trans-2,3-Dimethylthiirane + NH <sub>3</sub>	1.84		2.43	1.82	154	-57.5, 60.3, -179
Thiirane + Me <sub>2</sub> NH	1.83		2.37	1.82	163	65.3, -169, -51.9
2-Methylthiirane + NH <sub>3</sub> at C <sub>2</sub>	1.85		2.44	1.82	153	-53.0, 64.3, -174
2-Methylthiirane + NH <sub>3</sub> at C <sub>3</sub>	1.75		2.43	1.81	159	57.9, -59.7, 179

a) Distance in Angstroms.

b) NC<sub>2</sub>S Angle in degrees.