

**Table S1, Part B.** Total Energies of the Model Systems.<sup>a</sup>

Method	<b>CH<sub>3</sub>NO<sub>2</sub></b>	<b>CH<sub>3</sub>NO<sub>2</sub></b>	<b>H<sub>2</sub>CN(Me)O</b>	<b>H<sub>2</sub>CN(Me)O</b>	<b>E<sub>rel</sub></b>
	<i>eclipsed</i>	<i>staggered</i>	<i>syn</i>	<i>anti</i>	
	<b>E<sub>tot</sub></b>	<b>E<sub>tot</sub></b>	<b>E<sub>tot</sub></b>	<b>E<sub>tot</sub></b>	
RHF/6-31G*	-243.661983	-243.661992	-207.844341	-207.848528	2.63
MP2(full)/6-31G*	-244.345308	-244.345335	-208.474663	-208.477655	1.88
Becke3LYP/6-31G*	-245.009334	-245.009325	-209.108589	-209.111677	1.94
RHF/6-311G**	-243.729003	-243.729017	-207.900430	-207.904670	2.66
MP2(full)/6-311G**	-244.538989	-244.539018	-208.657642	-208.660644	1.88
Becke3LYP/6-311G**	-245.081535	-245.081539	-209.170347	-209.173342	1.88

(a) Total energies in atomic units. The relative energies are given in kcal/mol.

**Table S2.** Dipole Moments of Nitromethane and *N*-Methylformaldimine *N*-Oxide.<sup>a</sup>

Method	$\mu_x$	$\mu_y$	$ \mu $	$ \mu _{\text{NP}}$	$ \mu _{\text{MP}}$	$x \mu$	$\mu_y$	$ \mu $	$ \mu _{\text{NP}}$	$ \mu _{\text{MP}}$
	<b><i>ecl.</i>-CH<sub>3</sub>NO<sub>2</sub></b>					<b><i>stag.</i>-CH<sub>3</sub>NO<sub>2</sub></b>				
RHF/6-31G*	0.15	-4.01	4.01	5.45	5.92	-0.23	-4.01	4.02	5.45	5.92
MP2(full)/6-31G*	0.11	-3.43	3.43	4.77	4.98	-0.27	-3.42	3.43	4.77	4.97
Becke3LYP/6-31G*	0.09	-3.47	3.48	4.91	5.02	-0.19	-3.47	3.48	4.91	5.01
	<b><i>anti</i>-H<sub>2</sub>C=N(O)CH<sub>3</sub></b>					<b><i>syn</i>-H<sub>2</sub>C=N(O)CH<sub>3</sub></b>				
RHF/6-31G*	-3.40	-2.93	4.49	6.35	6.13	3.67	-2.52	4.45	6.31	6.01
MP2(full)/6-31G*	-2.03	-2.89	3.53	5.20	4.93	2.30	-2.65	3.51	5.19	4.83
Becke3LYP/6-31G*	-2.26	-2.76	3.56	5.37	4.94	2.47	-2.49	3.51	5.33	4.81

(a) Dipole moment in Debye. Nitromethane is oriented such that the C-N bond is aligned with the y-direction and the xy-plane is the symmetry plane for both conformations. The unique methyl H-atoms in the nitromethane structures are oriented in the positive x-direction.

(b) Abbreviations: NP = Natural Population, MP = Mulliken Population.