Detection and Identification of Reaction Intermediates in the Photorearrangement of Pyridazine *N*-Oxide: Discrepancies Between Experiment and Theory

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Supporting Information

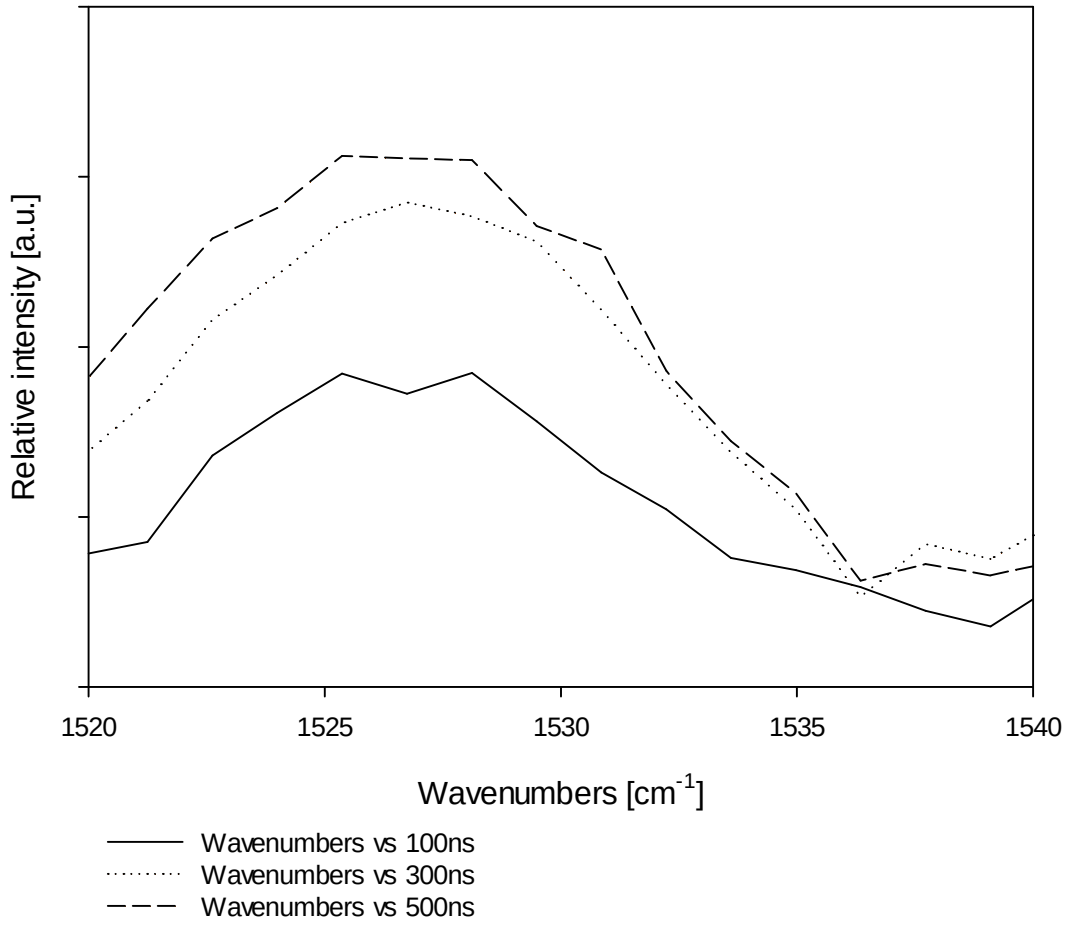

Figure S1: experimental ns-TR3 spectra observed after different time intervals after laser excitation of 5.

Table S1. Electronic energies (in Hartrees) for stationary points in the photochemical rearrangement of **5**. In brackets: energies (in kcal mol^{-1}), relative to E(**6**) = 0.0 kcal mol^{-1} (if a reference value for **6** is available). n.a.m: not a minimum. n.c.: not calculated.

Method	Basis set	E (**6**)	E (TS **6**→**7**)	E (**7**)	E (TS **7**→**8**)	E (**8**)
RHF	6-31G*	-337.387957 (0.0)	-337.373003 (9.4)	-337.410132 (-13.9)	-337.404829 (-10.6)	-337.459363 (-44.8)
RHF (CH_3CN)	6-31G*	-337.400986 (0.0)	-337.382928 (11.3)	-337.417310 (-10.2)	-337.411634 (-6.7)	-337.467412 (-41.7)
RHF (CCl_4)	6-31G*	-337.393615 (0.0)	-337.377354 (10.2)	-337.413315 (-12.4)	-337.407792 (-8.9)	-337.462773 (-43.4)
MP2	6-31G*	n.a.m.	-	n.a.m.	-	-338.468330
MP3	6-31G*	-338.414646 (0.0)	-337 .407903 (4.2)	-338.437590 (-14.4)	-338.436104 (-13.5)	-338.470285 (-34.9)
MP3	cc-pVTZ	-338.775837 (0.0)	-338.771849 (2.5)	-338.799472 (-14.8)	-338.798502 (-14.2)	-338.836152 (-37.9)
MP4 (SDQ)	6-31G*	-338.430189 (0.0)	-338.424901 (3.3)	n.a.m.	-	-338.489617 (-37.3)
MP4 (SDTQ)	6-31G*	n.a.m.	-	n.a.m.	-	n.c.
CCSD	cc-pVTZ	-338.781144 (0.0)	-338.776693 (2.8)	n.a.m.	-	n.c.
CCSD(T)	cc-pVTZ	-338.850387 (0.0)	-338.849802 (0.4)	n.a.m.	-	n.c.
CASSCF (8,8)	6-31G*	-337.514176 (0.0)	-337.502246 (7.5)	-337.537562 (-14.7)	-337. 530562 (-10.3)	-337.593460 (-49.8)
B3LYP	6-31G*	n.a.m.	-	n.a.m.	-	-339.465319
M06	cc-pVTZ	-339.292310 (0.0)	-339.291737 (0.4)	n.a.m.	-	-339.366552 (-46.6)
M06 (CH_3CN)	cc-pVTZ	-339.301327 (0.0)	-339.299432 (1.2)	n.a.m.	-	-339.373806 (-45.5)
M06 + 12 CCl_4	6-31G*	-22883. 805367 (0.0)	-22883. 804830 (0.3)	n.a.m.	-	n.c.
M06-2X	cc-pVTZ	-339.389587 (0.0)	-339.388804 (0.5)	n.a.m.	-	-339.455037 (-41.1)

Calculations: Electronic Energies (in Hartree)
General remarks: All stationary points (except for geometry optimizations using CCSD or CCSD(T)) were characterized by performing a vibrational analysis. All minima had exactly zero vibrational modes with imaginary frequency, and all transition states exactly one. The Cartesian coordinates are available via the .xyz file connected with this Supporting Information. For compounds **6**-**8** and the transition states connecting them, the electronic energies in Hartree are found in Table S1.

Transition state 6→9, electronic energy (M06/cc-pVTZ)
E(M06) = -339.257286

Transition state 6→9, electronic energy (MP3/cc-pVTZ)
E(MP3) = -338.7110328

Oxirane 9, electronic energy (M06/cc-pVTZ)
E(M06) = -339.3314917

Oxirane 9, electronic energy (MP3/cc-pVTZ)
E(MP3) = -338.8130358

Transition state 9→8, electronic energy (M06/cc-pVTZ)
E(M06) = -339.2789263

Transition state 9→8, electronic energy (MP3/cc-pVTZ)
E(MP3) = -338.7358986

Transition state 9→10, electronic energy (M06/cc-pVTZ)
E(M06) = -339.3293092

Transition state 9→10, electronic energy (MP3/cc-pVTZ)
E(MP3) = -338.8072455

1,3,4-Oxadiazepine 10, electronic energy (M06/cc-pVTZ)
E(M06) = -339.3475481

1,3,4-Oxadiazepine 10, electronic energy (MP3/cc-pVTZ)
E(MP3) = -338.8334259

Transition state 10→16, electronic energy (M06/cc-pVTZ)
E(M06) = -339.3104652

Transition state 10→16, electronic energy (MP3/cc-pVTZ)
E(MP3) = -338.7738245

Singlet carbene 16, electronic energy (M06/cc-pVTZ)
E(M06) = -339.3208097

Singlet carbene 16, electronic energy (MP3/cc-pVTZ)
E(MP3) = -338.782962