Evidence of Hydrogen Migration in an Alkylphenyldiazirine Excited States

Yunlong Zhang,^a Jacek Kubicki,^b and Matthew S. Platz^a*

^a Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio, 43210, U.S.A.

^b Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University, 85 Umultowska, Poznan 61-614, Poland

Platz.1@osu.edu

Table of Contents

Figure S2. Ultrafast LFP (350 nm) of 3-trideuteromethyl-3-phenyl diazirine (PhCN₂CD₃). The kinetic traces in (a) acetonitrile and (b) cyclohexane fitted by to a bi-exponential function.

Figure S4. Ultrafast LFP (350 nm) of 3-*iso*-propyl-3-phenyl diazirine (PhCN₂-*i*-Pr). The kinetic traces in (a) acetonitrile and (b) cyclohexane fitted by to a bi-exponential function.

Figure S5. Ultrafast LFP (350 nm) of 3-*tert*-butyl-3-phenyl diazirine (PhCN₂-*t*-Bu). The kinetic traces in (a) acetonitrile and (b) cyclohexane fitted to a bi-exponential function... 4

Ultrafast UV-vis pump-probe absorption measurements were performed using the home-built spectrometer at the Ohio State University described elsewhere.¹ Solution concentrations were adjusted to absorption of unity in a 1 mm cell. Sample solutions were excited in a stainless steel flow cell equipped with 1 mm thick CaF_2 windows. After passing the sample reference and probe beam were spectrally dispersed with a

polychromator and independently imaged on the detector. The pump pulse energy was about 4 μ J at the sample position. The entire set of pump-probe delay positions (cycle) is repeated at least three times, to observe data reproducibility from cycle to cycle. To avoid rotational diffusion effects, the angle between polarizations of the pump beam and the probe beam was set to the magic angle (54.7°). Kinetic traces are analyzed by fitting to a sum of exponential terms. All experiments were performed at room temperature.

Figure S1. Ultrafast LFP (350 nm) of 3-phenyl-3H diazirine (PhCN₂H). The kinetic traces in (a) acetonitrile and (b) cyclohexane fitted to a bi-exponential function.



Figure S2. Ultrafast LFP (350 nm) of 3-trideuteromethyl-3-phenyl diazirine (PhCN₂CD₃). The kinetic traces in (a) acetonitrile and (b) cyclohexane fitted by to a bi-exponential function.



Figure S3. Ultrafast LFP (350 nm) of 3-ethyl-3-phenyl diazirine (PhCN₂Et). The kinetic traces in (a) acetonitrile and (b) cyclohexane fitted by to a bi-exponential function.



Figure S4. Ultrafast LFP (350 nm) of 3-*iso*-propyl-3-phenyl diazirine (PhCN₂-*i*-Pr). The kinetic traces in (a) acetonitrile and (b) cyclohexane fitted by to a bi-exponential function.



Figure S5. Ultrafast LFP (350 nm) of 3-*tert*-butyl-3-phenyl diazirine (PhCN₂-*t*-Bu). The kinetic traces in (a) acetonitrile and (b) cyclohexane fitted to a bi-exponential function.



Figure S6. Global analysis of the transient spectra produced with ultrafast LFP (350 nm) in the 400 – 650 nm spectral range for PhCN₂CH₃ (left) and PhCN₂CD₃ (right) in cyclohexane. DAS (Decay Associated Spectra) and the lifetimes associated with each spectrum are shown. The S₁ state lifetimes (5.2 ± 0.3 ps for CH₃ and 6.7 ± 0.5 ps for CD₃) are consistent with the data in Table 1.



(1) Wang, J.; Burdzinski, G.; Gustafson, T. L.; Platz, M. S. J. Org. Chem. **2006**, *71*, 6221.