

Investigation of Nitrenes and Chirality in Cryogenic Matrices

Rowen, J.F.,² Beyer, F.,^{1*} Schleif, T.,² Sander, W.,² Merten, C.,²

*presenter

¹frederike.beyer@rub.de, Ruhr-Universität Bochum, Germany

²Ruhr-Universität Bochum, Germany

To examine the influence of paramagnetism on vibrational circular dichroism (VCD) spectra, the parent system 2-azidofluorene **1a** and its chiral derivative 2-azidofluoren-9-ol **1b** have been synthesized, deposited in different cryogenic matrices and submitted to various irradiation conditions with subsequent characterization by infrared (IR), ultraviolet/visible (UV/Vis) and electron paramagnetic resonance (EPR) spectroscopy. These experiments provide a sound foundation for future investigations on 2-azidofluoren-9-ol **1b** by matrix isolation VCD (MI-VCD) spectroscopy and the validity of the VCD theory for open-shell systems.

Both samples 2-azidofluorene **1a** and 2-azidofluoren-9-ol **1b** form their corresponding nitrenes **2a** and **2b** upon irradiation at 254 nm. Under matrix isolation conditions in inert argon matrices at 3-10 K the nitrenes adopt a triplet spin state comprising two unpaired electrons and are hence paramagnetic species. Further irradiation at 450 nm induces rearrangements of both nitrene species to form the respective diamagnetic benzazirine (**3a/b_{down/up}**) and ketenimine (**4a/b_{down/up}**) derivatives. These rearrangements have been found to be reversible as irradiation at 405 nm regenerates the triplet nitrenes. The photochemical conversions could be performed repeatedly.

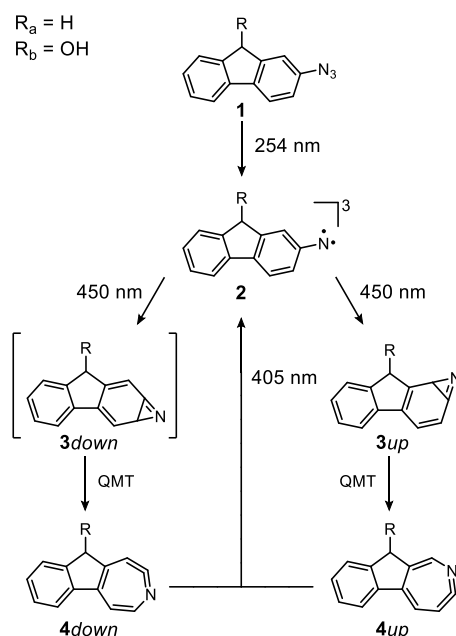


Figure 1: Photochemistry of azides **1a** and **1b**. Upon irradiation at 254 nm nitrenes **2a/b** form, which rearrange to ketenimines **4** via (intermediary) benzazirines **3** upon irradiation at 450 nm. Irradiation at 405 nm regenerates triplet nitrene.

In addition to this photochemical conversion, kinetic studies suggest the rearrangements also to happen via heavy-atom quantum mechanical tunnelling (QMT). These processes have been studied for the parent system 2-azidofluorene **1a** and revealed interesting differences in the behaviour of **3_{aup}** and **3_{adown}** regarding energy profiles and corresponding tunnelling probabilities.