

# Insights into the mechanism of the photoinduced Wolff rearrangement of diazonaphthoquinone

Quansong Li

## Abstract

Diazonaphthoquinone (DNQ) undergoes the light-induced Wolff rearrangement (WR), which is widely applied in the fabrication of photoresists. Based on the vertical excitation spectrum, the WR mechanism of DNQ has been determined by calculating the reaction paths on the ground and excited state potential energy surface at the CASPT2//CASSCF level. The minimum energy paths (MEPs) start from the Franck-Condon structure on the two lowest energy states of  $\pi\pi^*$  and  $\pi\pi^*_{\text{NN}}$  character. Both paths lead without a barrier to a conical intersection seam between the ground state ( $S_0$ ) and first excited state ( $S_1$ ). The  $S_1/S_0$  intersection seam is energetically accessible in experiments (with UV of 400 nm or between 300 and 350 nm) and from this seam different species can be formed: the final ketene product of the rearrangement, a carbene intermediate, a diazirine side product, and the reactant DNQ. According to our calculations, the photo-induced WR of DNQ may occur in a nonsynchronous concerted way or via a carbene intermediate. The comprehensive WR mechanism agrees well with previous experimental observations and may have important implications in organic synthesis and photoresists fabrication.