

2-Nitreno-9-fluorenylidene – A Quintet Ground State Carbenonitrene

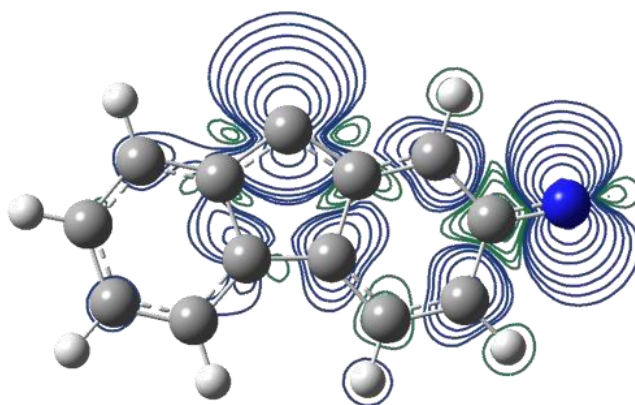
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Reactive intermediates such as carbenes and nitrenes have been the subject of many studies in physical organic chemistry during the past years. Due to their unpaired electrons in the triplet state these molecules might serve as promising candidates for the development of organic magnets. In order to increase the magnetic properties, molecules consisting of more than one spin center, like ferromagnetically coupled polycarbenes or polynitrenes have been investigated.¹ However, little research has been conducted on molecules where both a carbene and nitrene center are present. In this work, 2-azido-9-diazo fluorene and its photochemistry were investigated, yielding a molecule that couples these two moieties and thus provides insights into their unique intramolecular interactions.



Therefore, 2-azido-9-diazo fluorene was isolated in an argon matrix at 3 K and irradiated with UV light. By comparison of the obtained IR spectra with calculations, the formation of quintet ground state 2-nitreno-9-fluorenylidene was observed. Furthermore, the spin state was verified by X- and Q-band EPR spectroscopy. In order to investigate the kinetics of the quintet formation, transient absorption spectroscopic measurements in the ultraviolet and visible spectral region were performed. Comparison with literature data for 9-fluorenylidene² and 2-nitrenofluorene³ indicated the formation of a carbene and a nitrene center separated from each other. Thus, it can be concluded that the carbenonitrene is formed by a stepwise dissociation of two nitrogen molecules that requires the absorption of more than one photon.

¹ Mendez-Vega, E.; Mieres-Perez, J.; Chapyshev, S. V.; Sander, W. Persistent Organic High-Spin Trinitrenes *Angew. Chem. Int. Ed.*, **2019**, 58, 12994-12998.

² Wang, J.; Kubicki, J.; Hilinski, E. F.; Mecklenburg, S. L.; Gustafson, T. L.; Platz, M. S. Ultrafast Study of 9-Diazo fluorene: Direct Observation of the First Two Singlet States of Fluorenylidene *J. Am. Chem. Soc.*, **2007**, 129 (44), 13683-13690.

³ Wang, J.; Burdzinski, G.; Platz, M. S. Solvent Effects on Intermolecular Proton Transfer: The Rates of Nitrene Protonation and Their Correlation with Swain Acidity *Org. Lett.*, **2007**, 9 (25), 5211-5214.