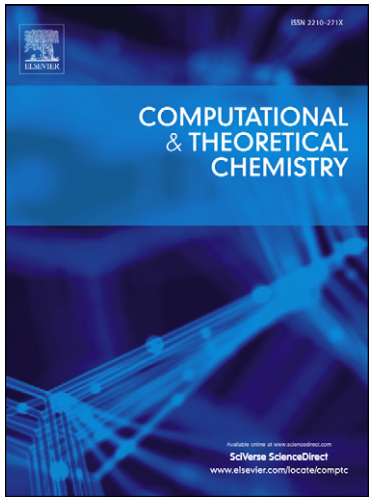

Carbenes and Nitrenes. An Overview

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Carbenes and Nitrenes. An Overview

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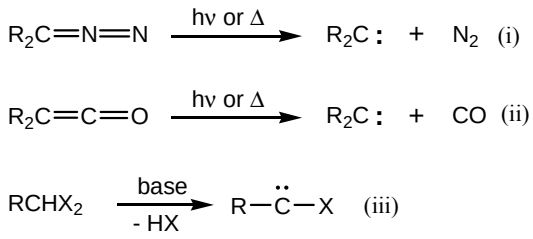
Abstract. A brief survey of the structure, methods of generation and reactivity of the singlet and triplet carbenes and nitrenes is given. The DFT and CCSD(T) calculations of the singlet–triplet energy gap ΔE_{ST} for a large number of differently substituted carbenes and nitrenes are performed and the dependence of ΔE_{ST} on the substituent(s) at the sextet center is discussed.

Keywords: carbenes · nitrenes · singlet–triplet energy gap · DFT · CCSD · CCSDT

1. Background

Carbenes and nitrenes are sextet, neutral, highly reactive molecular species with a divalent carbon atom or monovalent nitrogen atom, which can exist in a singlet or a triplet state [1]. Various aspects of the structure and chemical properties of these species are extensively discussed in the literature. Therefore, the purpose of the present paper is to give a brief survey of the methods of generation, the patterns of reactivity, and to discuss the dependence of the singlet–triplet gap in carbenes and nitrenes on the substituents at the sextet center based on both the literature and our own theoretical calculations.

There are three principal methods of generation of carbenes (in the order of increasing synthetical importance): (i) thermal or photochemical decomposition of diazo compounds; (ii) thermal or photochemical decomposition of ketenes, and (iii) base-promoted 1,1-elimination (Scheme 1):



Scheme 1 Principal methods of generation of carbenes

Singlet carbenes have the lone pair of electrons on the sp^2-hybridized σ-orbital and a bent structure with an RCR angle close to 120 (depending on R). Triplet carbenes may be either linear (when the two electrons occupy two different p-orbitals) or angular (when they occupy an