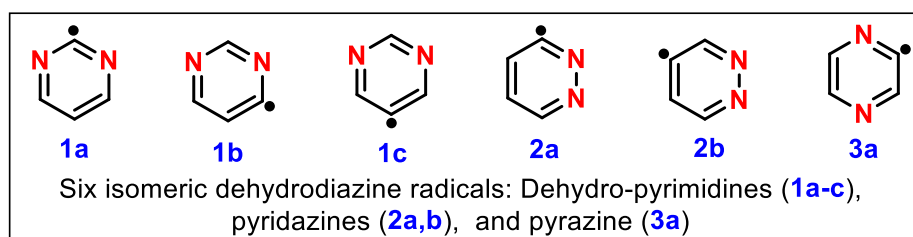


Abstract

Free radicals, in general, are highly reactive and short-lived chemical entities (intermediates) containing one or more unpaired electrons. Their importance is felt in many fields such as organic synthesis, biochemistry, medicinal chemistry, polymer chemistry, atmospheric chemistry, and interstellar chemistry, etc. Various strategies and methods have been adapted to tune and control the stability and in turn, reactivity of radicals that include the introduction of various heteroatoms that can be stabilizing/destabilizing the radicals. Recently, the studies on nitrogen-based heterocyclic radicals gained importance, as these moieties constitute the main building block of several biological systems (like nucleobases, amino acids, etc.), biologically active drug molecules, and are also potential precursors in prebiotic chemistry. Among the various *N*-heterocycles, diazines are those containing two nitrogen atoms that can be classified as pyridazine (1,2-diazine), pyrimidine (1,3-diazine), and pyrazine (1,4-diazine) depending on the relative position of the two nitrogens. Of all these diazine derivatives, pyrimidine (1,3-diazine) moiety has a significant role in biological compounds specifically in nucleobases such as cytosine, thymine, and uracil, which are the key building blocks of DNA and RNA.



Given their biological implications and their relevance in radical damage, systematic studies on diazine-based radicals are quite insightful, and equally intriguing from the fundamental point of view. Since all these radicals have one unpaired electron and two nitrogen lone pairs, the nature and strength of possible “3-centered – 5 electrons” (3c-5e) interactions may play a crucial role in their existence or non-existence, and also their inherent reactivity. To address these, we investigated the electronic structure and unimolecular reactivity aspects of these six-isomeric dehydrodiazine radicals using quantum chemical calculations, which provided the importance of through space (TS) and through bond (TB) interactions between the unpaired electron and the lone pair(s). Attempts have also been made towards the experimental characterization of such transient species using the matrix-isolation (MI) technique in combination with infrared spectroscopy and computations. Under photochemical conditions, we have successfully generated dehydro-diazine radicals (2-dehydropyrimidine

and 2-dehydropyrazine radicals from their respective iodo-precursors) in an inert gas matrix at cryogenic conditions (4 K). Moreover, the photochemistry of these diazine radicals has led to the ring-opening and ring-fragmented products, which have relevance in astrochemistry. Interestingly, several nitrogen rich ring-opened products with a molecular formula $C_4H_2N_2$ have been characterized, which are relevant to aza-enediyne antibiotics. Similarly, 4,6-diiodopyrimidine and 3,6-diiodopyridazine have been used to generate didehydrodiazines, which essentially led to ring-opened products. To shed further light on this, electronic structure of didehydrodiazine biradicals (4c-6e interaction) has also been investigated. Overall, the theoretical insights on the dehydro- and didehydrodiazine radicals, and the experimental results including the design of matrix isolation experimental set up will be presented.