MOLECULAR BASIS OF THE DNA/RNA DAMAGE BY UV LIGHT, REACTIVE OXYGEN SPECIES AND LOW-ENERGY ELECTRONS

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DNA/RNA nucleobases are known to be characterised by ultrafast decay channels, which make them photo-stable against UV radiation.[1] Nevertheless, lesions are experimentally observed in the DNA/RNA environment.[2] Two examples are the cyclobutane pyrimidine dimers (CPDs) and the tautomers of the nucleobases. In addition to the UV light, reactive oxygen species (ROS) and low-energy electrons are also frequent sources of damage to the nucleic acids. During the last decade, we have performed photochemical reaction-path computations using multiconfigurational quantum chemistry to determine the mechanisms of the aforementioned DNA/RNA lesions. On the basis of the results obtained, we could rationalise the different quantum yields of formation of CPDs[3] and describe the thermal and photochemical inter-conversion between the canonical and tautomeric nucleobases.[4] Moreover, we have determined the absorption properties of the transient radicals formed by the ROS addition to the pyrimidines and we have explored the photochemistry of these adducts.[5] In this context, we have found photochemical routes that regenerate the canonical nucleobases. These channels are accessible by irradiation of visible light and therefore might imply a photo-protection mechanism. For the interaction between the nucleobases and low-energy electrons, we have described the role of dipole- and valence-bound anionic states of the bases and the distinct behaviour of guanine as compared to adenine and the pyrimidines.[6] In this contribution, we will briefly summarise the findings obtained and comment on their relevance in the field of DNA/RNA damage.

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