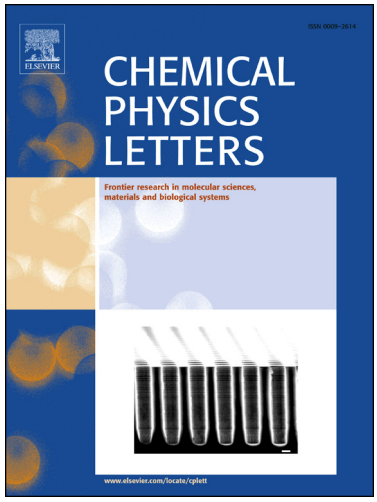

Research paper

Evolution of electron density towards the conical intersection of a nucleic acid purine

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PII: S0009-2614(17)30241-5
DOI: http://dx.doi.org/10.1016/j.cplett.2017.03.021
Reference: CPLETT 34621

To appear in: *Chemical Physics Letters*

Received Date: 9 January 2017
Revised Date: 7 March 2017
Accepted Date: 8 March 2017

Please cite this article as: L. Gutiérrez-Arzaluz, D. Ramírez-Palma, F. Buitrón-Cabrera, T. Rocha-Rinza, F. Cortés-Guzmán, J. Peón, Evolution of electron density towards the conical intersection of a nucleic acid purine, *Chemical Physics Letters* (2017), doi: http://dx.doi.org/10.1016/j.cplett.2017.03.021

Evolution of electron density towards the conical intersection of a nucleic acid purine

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Abstract

We analyzed the evolution of the electron density across the S_0 and S_1 states potential energy curves of hypoxanthine (Hx) using the Quantum Theory of Atoms in Molecules (QTAIM). Examination of QTAIM energies and electronic populations indicates that charge transfer processes are important in the stabilization of the S_1 state towards the Conical Intersection (CI) which confers to Hx its photostability. Our results point that the rise of energy of the S_0 state approaching the CI is accompanied by a loss of aromaticity of hypoxanthine. Overall, the analyses presented herein give important insights on the photostability of nucleobases.

Keywords

DNA bases, excited states, TDDFT, Quantum Chemical Topology, electron density, conical intersections.

Introduction

Individual DNA bases have significant UV absorption cross sections of the order of 8 000 to 15 000 M^{-1} cm^{-1}. Despite this feature, these chromophores show an intrinsic photostability due to the presence of remarkable molecular mechanisms which efficiently eliminate the electronic energy associated with photon absorption.[1] Such mechanisms have been associated with natural selection processes at the molecular level which probably contributed to isolate highly photostable chromophores in the earliest stages of the evolution for organic compounds to make up the genetic material. [2–5]

The photostability of the four natural DNA bases and of several similar purines and pyrimidines is due to ultrafast photophysical processes in which one or a series of conical