"III Congreso Latinoamericano de Astrobiología (2021)"
Revista Mexicana de Astronomía y Astrofísica Serie de Conferencias (RMxAC), **55**, 102–102 (2023)

https://doi.org/10.22201/ia.14052059p.2023.55.38

A COMPARISON OF THE SPECTROSCOPIC AND THERMODYNAMIC PROPERTIES OF CHLOROPHYLLS AND BACTERIOCHLOROPHYLLS WITH AN EVOLUTIONARY PERSPECTIVE

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This paper shows preliminary results on changes of the UV-Vis spectroscopic and thermodynamic properties in the chlorophyll and bacteriochlorophyll stereoisomers.

Chlorophylls and bacteriochlorophylls are the main photosynthetic pigments (Senge Mathias O. et al. 2014). They absorb energy from different wavelengths such as the visible emitted by the sun and the near infrared at hydrothermal vents. These molecules transform this radiation energy into chemical energy. These pigments are present in both oxygenic and anoxygenic photosynthesis and are characterized by having one or more chiral centres, namely, optically active. Currently, it is still unknown if chirality went through a pre-biological selection at a molecular level and stabilized these photopigments. Therefore the main question is whether or not this molecular selection occurred on ancient Earth "choosing" epimers from the photosynthetic pigments.

Molecular sructuctures were imported from the Protein Data Bank (PDB) and others were built using Hyperchem (8.0.5 Hypercube, inc.). Subsequently, epimers for the chiral centres C3A (Chlorophyll *a*) and CAB (Bacteriochlorophyll *f*) were generated. The minimum internal energy (U) was used to infer the most stable structure of the molecules after an energy optimization in molecular mechanics (Mm+). Also, the UV/Vis spectra were obtained with the semi-empirical method ZINDO/S in Single Point CI configuration after the Mm+ optimizations.

Chiral centres from Chl *a* and BChl *f* are shown in Fig. 1. Depending of the molecule configuration, either "R" or "S", the functional groups linked to the chiral centres are symetrically inverted.

Preliminary results show different data for the lowest energies and the UV-Vis spectra. The energy obtained for the R-configuration C3A chiral centre is $\sim$ 180.556 kcal/mol, whereas for the S-configuration

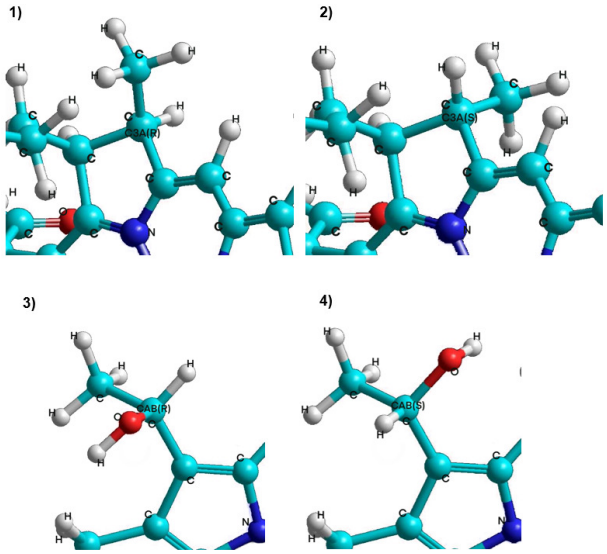

Fig. 1. Chiral centres 1) C3A (R), 2) C3A (S) for Chl *a* and 3) CAB (R), 4) CAB (S) for BChl *f*.

the energy is $\sim$ 177.096 kcal/mol, being this one the most stable form with an energy difference of $\sim$ 3.455 kcal/mol between them. Bacteriochlorophyll *f* CAB chiral centre shows a difference between the "R" and "S" configuration of just 0.015627 kcal/mol.

Differences between epimers pigments can also be observed in the UV-Vis spectra. The absorption bands of BChl *f* presents small changes compared to Chl *a*. According to Fujita (2015) and Kinoshita et al. (2015) it has been proved the functionality of both epimers "R" and "S" of BChl *f* in *Chlorobaculum limnaeum*, a green sulfur bacterium (GSB). This might explain the low differences in epimer internal energies, therefore, contributes to sustain the hypothesis of a "racemic ancestral bacteriochlorophyll" subsequently selected on advanced stages in photosynthesis evolution.

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