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A theoretical analysis of the intrinsic light-harvesting properties of xanthopterin

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ABSTRACT

Belonging to the family of pterins, which are common chromophores in several bio-organisms, xanthopterin has been shown experimentally (Plotkin et al., 2010) to have the ability of acting as a light-harvesting molecule. In the present study, multiconfigurational second-order perturbation theory is used to determine the stability of distinct amino/imino and lactam/lactim tautomers and the absorption and emission spectroscopic characteristics, electron donor and acceptor properties and the electron and charge transfer efficiencies via π-stacking. The lactam–lactam form 3H5H (and in a lesser extent 1H5H) is predicted to have the most appropriate intrinsic characteristics for the light-harvesting properties of xanthopterin, since it is the most stable isomer predicted for the gas phase and estimated for polar environments, absorbs solar light at longer wave lengths, has relatively low donor properties and the presence of the keto groups, instead of enol, increases the efficiency for energy transfer through excimer-like interactions.

1. Introduction

Xanthopterin is a yellow pigment commonly found in the wings of certain butterflies and in the urine of mammals [1]. This heterocyclic compound belongs to the family of pterins (see Fig. 1), which are widely spread molecules in living organisms [2]. Pterins participate in relevant biological functions as, for example, natural pigments (xanthopterin, leucopterin) [3] or coenzymes in the synthesis of purine and pyrimidine bases (folic acid) [4] and the metabolism of some amino acids (tetrahydrobiopterin) [5]. The participation of pterins in different photobiological processes as antennas in plants and insects has been also suggested [6–8]. This fact has increased the interest in the photophysics and photochemistry of the compounds. In 2010, Plotkin et al. [8] analysed the biophysical properties of the yellow-coloured cuticle of the Oriental hornet (*Vespa orientalis*), which contains xanthopterin, to absorb solar light and transform it into chemical energy. In addition, an organic solar cell was constructed using xanthopterin as dye, which showed a conversion efficiency of 0.335% [8]. It is impressive that despite the fact that the value is small in comparison to the typical synthetic dyes employed nowadays, the molecule still shows the ability of collecting solar light and converting it into electrical energy. To understand the light-harvesting properties of the molecule, knowledge of the chemical structure, the characteristics of the excited states and the donor, acceptor, energy transfer and charge transfer properties of xanthopterin is crucial.

Different isomers of xanthopterin have been presented in the literature, corresponding to amino/imino and lactam/lactim tautomers. It is worth noting that the two rings of the molecule contain cyclic amides which can exist in either lactam (keto) or lactim (enol) forms (see Fig. 2). In addition, amino/imino tautomerism is also possible at ring A, giving rise to the protonated forms at positions N_1 and N_3. Xanthopterin was introduced by Lorente and Thomas [2] as the 6-hydroxypterin (isomer 3H6H). Meanwhile, Plotkin et al. [8] referred to the N_1-amino and C_4- and C_6-keto form (isomer 1H5H) in the analysis of the performance of a xanthopterin-sensitised solar cell. In other works, the 2-amino-4,6-dihydroxypteridine term is used (see [9] and references therein). The six isomers shown in Fig. 2 might have distinct abilities for absorbing solar radiation and initiating a chain of processes to convert photons into chemical (or electrical) energy, which to our knowledge has not been theoretically studied before.

Hence, in the present work we use the complete-active-space second-order perturbation theory//complete-active-space self-consistent field (CASPT2//CASSCF) method [10–14] to analyse

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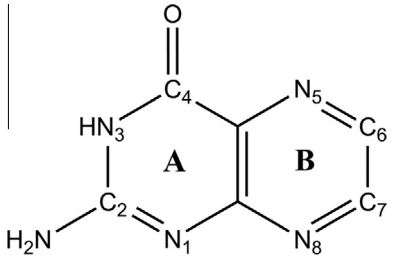

Fig. 1. Molecular structure of 2-aminopteridin-4(1*H*)-one or pterin. Pterin derivatives usually found in Nature are C_6-substituted compounds (see [2] and references therein); an hydroxyl (OH) group in case of xanthopterin.

the molecular basis of xanthopterin as light-harvesting molecule. The following systematic approach is employed: first, the most stable isomers are determined among the most plausible forms proposed in the literature, second, the absorption and emission theoretical energies are computed and analysed, and finally, the electron donor and acceptor properties as well as the relative efficiencies for energy transfer (ET) and charge transfer (CT) are studied. For this purpose, several theoretical quantities are computed here for all the isomers of xanthopterin and in the homodimers formed by two identical molecules placed in a face-to-face orientation (see Fig. 3). For the monomers, we determine the vertical electronic absorption energies (E_{VA}) of the three lowest-lying $\pi\pi^*$ excited states, the vertical electronic emission energies (E_{VE}) and the adiabatic electronic band origin (T_e) of the lowest-lying $\pi\pi^*$ excited state (S_1), the vertical ionisation potentials (*VIP*) of the neutral systems and the vertical attachment energies (*VAE*) of the cationic systems produced after ionisation. For the homodimers, the electronic couplings for ET (H'^{ET}) and CT (H'^{CT}) are obtained by means of the computation of the energy splitting of the two lowest-lying excited and two lowest-lying cationic states, respectively. A comparative analysis of the theoretical properties is provided which allows determining the relevance of the isomers for the light-harvesting characteristics of xanthopterin.

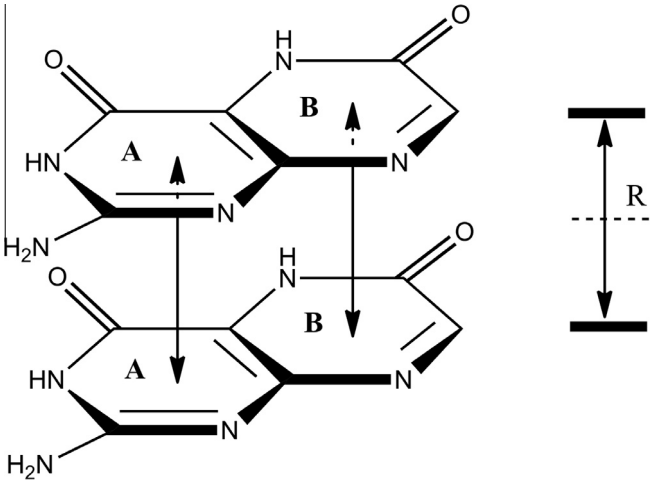

Fig. 3. Scheme of two xanthopterin 3H5H molecules showing the face-to-face arrangement of the homodimers considered in the present study. The dashed line represents the mirror symmetry plane of the homodimers. *R* stands for the intermolecular distance.

2. Computational details

Below, first, the methodologies employed to characterise the electronic structure are described. Second, the approximate procedure to estimate the efficiency for the ET and CT processes in homodimers of the xanthopterin isomers is explained in detail.

2.1. Electronic-structure methods

The coupled cluster singles doubles and perturbative triples// coupled cluster singles doubles [CCSD(T)//CCSD] and CASPT2// CASSCF methodologies have been employed in the present work together with the double-ζ quality basis sets of Dunning type cc-pVDZ and of atomic natural orbital (ANO) S-type with the contraction scheme C,N,O[321]/H[21], respectively. The ground-state

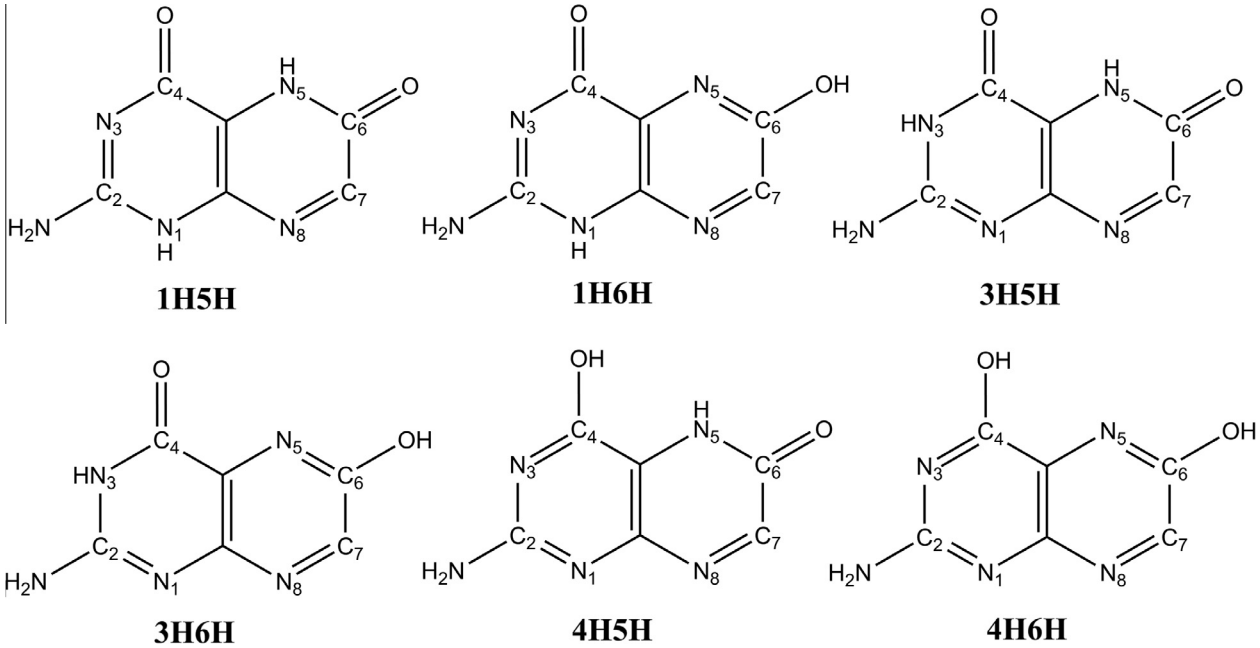

Fig. 2. Lactam/lactim and amino/imino tautomers of xanthopterin.