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.

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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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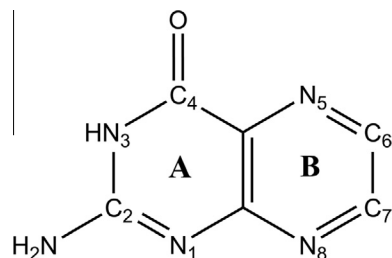*E-mail address:* Daniel.roca@uv.es (D. Roca-Sanjuán).

Fig. 1. Molecular structure of 2-aminopteridin-4(1H)-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.

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.

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.
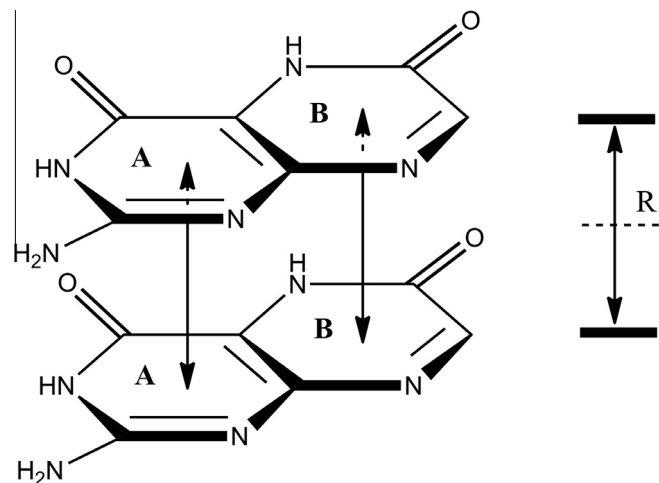
2. Computational details

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
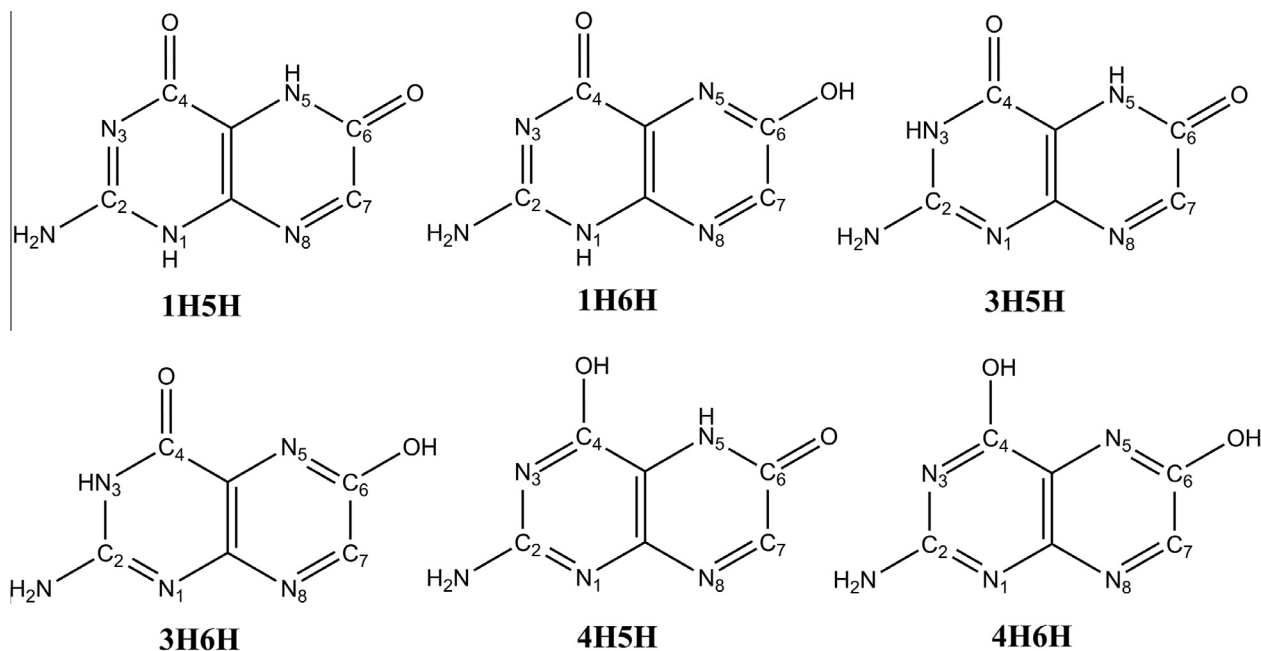

Fig. 2. Lactam/lactim and amino/imino tautomers of xanthopterin.

equilibrium structures of the xanthopterin neutral isomers have been optimised with the CCSD and CASSCF methods. Cationic structures have been optimised only with the latter method. CCSD(T) and CASPT2 energy corrections have been obtained subsequently at the CCSD and CASSCF geometries, respectively, for the analysis of the stability of the isomers. The CASPT2 method has been also employed to compute the E_{VA}, E_{VE}, T_e, VIP and VAE energies of the isomers, as well as the H'^{ET} and H'^{CT} couplings of the homodimers. Four singlet states have been averaged in the CASSCF computations of E_{VA}, E_{VE} and T_e, and two doublet states for those of H'^{ET} and H'^{CT}. In the case of VIP and VAE, state-specific CASSCF calculations have been carried out with one singlet and one doublet state. In order to minimize the effect of weak intruder states in the CASPT2 calculations, the parameter of the imaginary level-shift has been fixed to 0.2 au [15]. A modified zeroth-order Hamiltonian especially suited to correct systematic errors in open-shell systems [ionisation potential electron affinity (IPEA) parameter with a value of 0.25] [16] has been used for the VIP, VAE and H'^{CT} calculations in both the neutral and cationic systems, since it has been previously shown that it improves results of electron donor and acceptor properties in related compounds [17–19]. The remaining CASPT2 calculations (in neutral systems) have been performed with the conventional zeroth-order Hamiltonian as originally implemented (IPEA = 0.0). Core orbitals have been kept frozen. Single-reference CC computations have been carried out by the GAUSSIAN 09 quantum-chemistry software package [20], while the MOLCAS 7 program [21,22] has been used for the multiconfigurational CASPT2//CASSCF calculations.

Two sets of orbitals have been used in the active space of the CASPT2//CASSCF calculations. For the monomers, the valence π orbitals of the molecules are considered, with the exception of the out-of-plane lone-pair orbitals of the external amino (NH_2) and hydroxyl (OH) groups. Hence, in the case of close-shell calculations (neutral systems) it corresponds to 14 electrons and 12 orbitals, 12 electrons and 11 orbitals, 14 electrons and 12 orbitals, 12 electrons and 11 orbitals, 12 electrons and 11 orbitals, and 10 electrons and 10 orbitals, for 1H5H, 1H6H, 3H5H, 3H6H, 4H5H and 4H6H, respectively. One electron is removed in the open-shell calculations (cations). Regarding the dimers, the active space per molecule has been reduced to the three π and three π* most relevant orbitals, resulting therefore in an active space for the dimer of 12 electrons distributed in 12 orbitals in the neutral systems and 11 electrons distributed in 12 orbitals in the cations. Due to the truncation, the results obtained can only be used for a qualitative comparison of the electronic coupling between the states considered.

Additional test calculations have been performed increasing the active space with the inclusion of the out-of-plane lone-pair orbitals of the external amino and hydroxyl groups and enlarging the basis set to the ANO-L type with the contraction scheme C,N,O[4s3p1d]/H[2s1p].

2.2. Electronic-coupling calculations

The calculation of the electronic coupling matrix element H' between two states inter-converted by the energy or charge transfer processes is the crucial part in the determination of the related ET and CT rates and lifetimes, via an appropriate golden rule expression, $k = \frac{4\pi^2}{h} H'^2 FC$, where FC is the Franck–Condon factor [23].

The extent of the H' coupling controls the ET and CT processes, specifically the passage from one state to another and it can be taken as a measure of its efficiency. Different procedures to estimate the couplings have been developed [23–26] based on diabatic localised dimer calculations, monomer transition densities or transition dipole moments, and a super-molecule ansatz of the dimer

[27]. Other works and strategies are worth mentioning: see Refs. [28–31]. From all procedures, we will employ an energy gap-based method, such as the super-molecule dimer approach, in which the value of the coupling is obtained as half the splitting or perturbation between the interacting states, shown previously to be convenient to comparatively analyse the extent of ET and CT processes in related compounds [32,33]. Therefore, the computed H'^{ET} and H'^{CT} electronic couplings are obtained as $\frac{1}{2}|\Delta E_{ET}|$ and $\frac{1}{2}|\Delta E_{CT}|$, respectively. In these expressions, the energy differences ΔE_{ET} and ΔE_{CT} between the two lowest-lying ππ* excited states and the two lowest-lying cationic states, respectively, are calculated at a distance R between the monomers of 3 Å (see Fig. 3), keeping for each molecule the optimised geometry of the ground state. Notice that the basis set superposition error (BSSE) does not affect the results of the coupling, which uses energy differences between states computed at the same geometry [32,33].

3. Results and discussion

The results are presented in three sections. First, determination of the most stable isomers of xanthopterin is considered. Second, the absorption and emission spectroscopic characteristics of the isomers are analysed and compared. Third, the electron donor and acceptor energies of the isomers and the electronic coupling between monomers are studied and the relevance of the resulting values for the ET and CT processes is discussed.

3.1. Stability of xanthopterin isomers

Determination of the relative stability of the isomers of xanthopterin is predicted from the results obtained at the CCSD(T)// CCSD/cc-pVDZ and CASPT2//CASSCF/ANO-S 321/21 levels of theory. Table 1 compiles the obtained in-vacuo relative energies and the dipole moments computed with the CCSD and CASSCF methods. Deviations between the CCSD(T) and CASPT2 results for the energies are relatively small, with an average difference of 1.8 kcal/mol and the largest discrepancy of 3.0 kcal/mol appearing in the 4H6H isomer. Both methodologies show similar trends. The most stable compound is 3H5H, which corresponds to the keto forms at both C_4 and C_6 positions and the amino tautomer at position N_3. The isomers 3H6H, 4H5H and 4H6H follow at close energies up to 4 kcal/mol and 1 kcal/mol at the CCSD(T) and CASPT2 levels, respectively. Therefore, according to the small relative energy, all these species are expected to be present in some extent in the gas phase. Protonation at position N_1 give rise to less stable isomers (1H5H and 1H6H). Regarding lactam/lactim tautomerism, lactam forms are shown to be around only 1–2 kcal/mol more stable than the lactim forms, which can be explained by the amide-type resonance only possible in the former [9].

In polar media, changes in the stabilization of the isomers can be roughly estimated by the analysis of the dipole moments (μ).

Table 1
Energies (ΔE, in kcal/mol) of the ground-state equilibrium structures of the xanthopterin isomers relative to the most stable form (3H5H) and dipole moments (μ, in D) obtained at different levels of theory.

	ΔE		μ	
	CCSD(T)//CCSD	CASPT2//CASSCF	CCSD	CASSCF
1H5H	5.1	4.9	7.57	5.91
1H6H	8.4	6.3	6.41	5.23
3H5H	0.0	0.0	6.36	4.94
3H6H	2.1	0.7	3.22	2.36
4H5H	2.8	0.6	4.55	3.80
4H6H	4.0	1.0	2.39	2.15

Both CCSD and CASSCF give rise to the same ordering of values, with deviations in all cases lower than 1.7 D. According to the μ results, the most stable isomer predicted for the gas phase (3H5H) is estimated to maintain the stability also in polar solvents with no strong direct interactions with the solute. The relatively unstable 1H5H isomer in the gas phase has the largest μ value and therefore the population probability of this species is expected to increase approaching that of the 3H6H, 4H5H and 5H6H, which at the same time decrease the stability in comparison to the in-vacuo results. Hence, solvent effects on the tautomeric forms can be expected as follows: lactam forms at both A and B rings of the pterin structure possess larger μ values and therefore might be slightly stabilized; and the amino forms at position N_1 might increase stability since they have the largest values of dipole moment.

In summary, the most stable isomer of xanthopterin is predicted to be 3H5H in the gas phase and it might also be estimated as the most stable in polar environments. The N_1-imino isomers are expected to be populated in some extent in the gas phase and the B ring lactams in polar solvents.

3.2. Absorption and emission spectra

The E_{VA} transitions to the three lowest-lying $\pi\pi^*$ excited states, the E_{VE} emission energies from the equilibrium-structure of the S_1 $\pi\pi^*$ state and the band origin T_e have been determined at the CASPT2//CASSCF/ANO-S 321/21 level for the six isomers of xanthopterin. Tables 2 and 3 compile the energy values, oscillator strengths (f) of the transitions, dipole moment modules relative to that of the ground state ($\Delta\mu$) and the radiative lifetime (τ_{rad}) for the emission process.

The three groups of vertical transition energies, E_{VA}, computed at the CASPT2 level are placed at the energy ranges of 3.31–3.76, 4.66–5.18 and 4.79–5.88 eV (see Table 2). Hence, the lowest-energy range of electronic transitions are clearly separated from the other group of E_{VA} (at least 1 eV lower), whereas the transitions related to S_2 and S_3 show overlapping energy ranges of the E_{VA} values. In average, the second set of transitions show the highest values of oscillator strength. Experimentally, the absorption spectra of xanthopterin in water solution at pH 2.9 and 7.1[1] show two broad bands with band maxima at 390 and 280 nm (3.17 and 4.42 eV), being the second the strongest band [34]. These features in the absorption spectra can be ascribed to the two groups of electronic transitions of $\pi\pi^*$ character. In comparison to the experimental data, the CASPT2 results in vacuo slightly overestimate the energy of the transitions. Test calculations in 3H6H at the higher levels of theory CASPT2//CASSCF(16in13)/ANO-S 321/21 and CASPT2//CASSCF(12in11)/ANO-L 431/321 give rise to results that only differ from the present values by less than 0.1 eV and 0.03 eV in the case of the active space and basis set calibrations, respectively. Therefore, the reason of the overestimation can be found in the solvatochromic effects caused by water. This is confirmed by the $\Delta\mu$ analysis, which allows an estimation of the shifts caused by the polar solvent. Hence, the S_1 excited state possesses similar or larger μ values (up to ∼2 D) than those of the ground state, which implies a red shift of the transition energies, approaching therefore the experimental value (3.17 eV) [34]. The S_2 state has both larger and lower relative μ values depending on the isomer, with a predominance of the larger μ (the differences with respect to the ground state are up to ∼3 D and 1.6 D, respectively). For the transitions related to the highest-energy excited state computed in vacuo, red shifting can be also expected (see $\Delta\mu$ values in Table 2).

Isomer contributions to the absorption bands recorded experimentally can be obtained from the comparative analysis of the data compiled in Table 2. For the lowest-energy band (band maximum at 3.17 eV) [34], the 3H5H isomer is predicted as the main responsible, taking into account that 3H5H has the lowest transition energy (3.31 eV) and the largest estimated solvatochromic red shift in polar solvents. This agrees with the fact that the molecule is the most stable isomer according to the analysis performed in the previous section. The 4H5H isomer, with an energy transition of 3.38 eV and an estimated solvatochromic red shift, can also contribute to the band maxima. The strongest band of the spectra (band maximum placed at 4.42 eV) [34] can be ascribed mainly to the 3H5H and 3H6H isomers, which have electronic transition energies of 4.66 and 4.75 eV, respectively, and the largest values of oscillator strength. Blue and red shifts caused by polar solvent effects are estimated for both isomers, respectively, which might increase the band width. The electronic transition to S_3 of 3H5H might also contribute to the band since it is almost degenerated with the transition to S_2 and a solvatochromic red shift can be expected for the former. In fact, the energy position of the second- and third-energy transition might be exchanged in polar solvents. Regarding the highest-energy electronic transition E_{VA} considered here, energies and f values indicate that the 4H6H compound can contribute significantly at energies higher than ∼5 eV.

From the aforementioned electronic transition energies, only those related to the S_1 $\pi\pi^*$ excited state appear in the visible (Vis) region of the electromagnetic spectrum and therefore shall be relevant for the light-harvesting properties of xanthopterin. The theoretical absorption band origin, T_e, is computed at 2.75 eV, which agrees with the experimental value [34]. The band covers therefore the highest-energy part of the Vis electromagnetic spectrum, giving rise to a yellow compound. The isomers absorbing mainly in the Vis region are the lactam (keto) forms of ring B, which have E_{VA} and T_e values 0.3–0.4 eV lower than those for the lactim isomers. In contrast, the lactam/lactim and amino/imino

Table 2
Vertical electronic absorption energies (E_{VA}, in eV), associated oscillator strengths (f) and relative dipole moment modules ($\Delta\mu$, in D) of the lowest three excited states computed for the xanthopterin isomers at the CASPT2//CASSCF/ANO-S 321/21 level of theory.

	S_1			S_2			S_3		
	E_{VA}[a]	f	$\Delta\mu$	E_{VA}[a]	f	$\Delta\mu$	E_{VA}[a]	f	$\Delta\mu$
1H5H	3.36	0.096	−0.29	4.80	0.013	−0.78	5.08	0.083	0.77
1H6H	3.68	0.101	−0.14	4.97	0.056	2.12	5.01	0.042	0.80
3H5H	3.31	0.071	2.12	4.66	0.214	−1.64	4.79	0.067	2.64
3H6H	3.76	0.068	2.16	4.75	0.231	2.86	5.28	0.006	4.93
4H5H	3.38	0.068	1.24	4.71	0.055	1.89	5.27	0.005	0.08
4H6H	3.70	0.065	1.19	5.18	0.010	0.39	5.28	0.102	3.64

[a] Experimental band maxima from Ref. [34]: 390 and 280 nm (3.17 and 4.42 eV).

Table 3
Vertical electronic emission energies (E_{VE}, in eV), adiabatic electronic band origin (T_e, in eV), and emission radiative lifetime (τ_{rad}, in ns) of the lowest-lying S_1 excited state computed for the xanthopterin isomers at the CASPT2//CASSCF/ANO-S 321/21 level.

	E_{VE}	T_e[a]	τ_{rad}
1H5H	2.60	2.83	39
1H6H	3.16	3.20	23
3H5H	2.41	2.80	61
3H6H	3.19	3.22	32
4H5H	2.45	2.75	57
4H6H	3.03	3.10	35

[a] Experimental band origin from Ref. [34]: ∼460 nm (∼2.69 eV).

[1] The pK_a values of xanthopterin are 6.25 and 9.23, which are assigned to the ionization of the 6-hydroxy and 4-hydroxy groups, respectively [9] A. Albert, The pteridines, Q. Rev. 6 (1952) 197–237.

tautomerism at ring A does not affect significantly the E_{VA} and T_e results (changes in all cases lower than 0.1 eV). In comparison to pterin and other pterin derivatives [2,35], the band absorption of xanthopterin is red-shifted around 0.4 eV. According to the present analysis, we ascribed this effect to the possibility of forming the lactam tautomer in ring B of the molecular structure of xanthopterin in contrast to the other compounds.

Absorbance in the Vis range is crucial for the role of xanthopterin as solar light antenna in the bio-organism in which the molecule is present. As explained in the introduction, in order to show the solar energy harvesting properties of the molecule in the epicuticle of the Oriental hornet, Plotkin et al. [8] prepared a dye-sensitised solar cell using xanthopterin as dye. The authors refer to the 1H5H molecular structure in their analysis, probably suggesting the N_3 and the oxygen atom of the C_4=O group as plausible anchoring positions to the TiO_2 surface. However, no reasons were provided for this selection. To understand the properties as dye in the solar cell, the analysis of the electron density shifts induced upon light excitation to the lowest-lying $\pi\pi^*$ excited state may be helpful. It can also be important for shedding light on the possible biological function of xanthopterin in preventing oxidative formation of melanin (the skin-pigment) through a chelation process with divalent metals [9,36]. As can be seen in Fig. 4, among the most stable isomers and those absorbing light at lower energies (1H5H, 3H5H and 4H5H), a directional electron-density promotion from ring A to ring B is shown in 1H5H and 3H5H. Hence, anchoring the molecule to the TiO_2 surface might be expected to be more efficient for the mentioned isomers in the atoms of ring B containing lone pairs, especially the N_8 atom where the negative charge is increased significantly upon excitation to the S_1 state. Another factor relevant for the efficiency of the process of electron donation to the surface is the decrease of the quantum yield of other decay processes. Radiative fluorescence lifetimes computed at the CASPT2//CASSCF/ANO-S 321/21 show the largest value for 3H5H, which is 20 ns higher than that of 1H5H. Hence, fluorescence decay channel is expected to be less relevant in the former isomer. The aforementioned characteristics point to 3H5H as a more efficient molecular structure for collecting solar light, as compared to 1H5H.

3.3. Electron donor and acceptor properties and energy and charge transfer

Determination of the electron donor properties (*VIP*) of xanthopterin and the electron attachment energies (*VAE*) of the resulting cationic systems have been computed at the CASPT2//CASSCF/ANO-S 321/21 level of theory for all the isomers. ET and CT relative efficiencies have been estimated from the electronic couplings H'^{ET} and H'^{CT} also determined with the CASPT2 method. The obtained results are reported in Table 4.

As for the electronic absorption and emission energies, the *VIP* is found to be lower for the lactam forms of ring B (1H5H, 3H5H and 4H5H). In this case, the average energy difference is 0.20 eV. The effect of lactam/lactim tautomerism of ring A in the ionisation process is smaller, presenting differences of *VIP* not larger than 0.10 eV. On the other hand, amino forms at the N_1 position give rise to larger *VIP* values, with an average deviation of 0.21 eV. Test computations in 3H6H at the CASPT2//CASSCF(12in11)/ANO-S 321/21 and CASPT2//CASSCF(16in13)/ANO-L 321/21 levels give rise to *VIP* values with small deviations with respect to the present results, in all cases lower than 0.1 eV. Since the *VIP* differences for the isomers are not large (see Table 4) and the CASSCF wave functions for the cationic systems show in some cases certain

Table 4
Vertical ionisation potentials (*VIP*) of the neutral systems, vertical attachment energies (*VAE*) of the cationic systems and H'^{ET} and H'^{CT} electronic couplings of the two lowest-lying excited and two lowest-lying cationic states of the homodimers computed for the xanthopterin isomers at the CASPT2//CASSCF/ANO-S 321/21 level. All values are in eV.

	VIP	*VAE*	H'^{ET}	H'^{CT}
1H5H	8.59	8.03	0.8	0.5
1H6H	8.90	8.32	0.6	0.6
3H5H	8.42	7.59	0.9	0.6
3H6H	8.65	7.77	0.7	0.6
4H5H	8.40	7.58	0.5	0.6
4H6H	8.55	7.76	0.5	0.6

1H5H   **1H6H**   **3H5H**
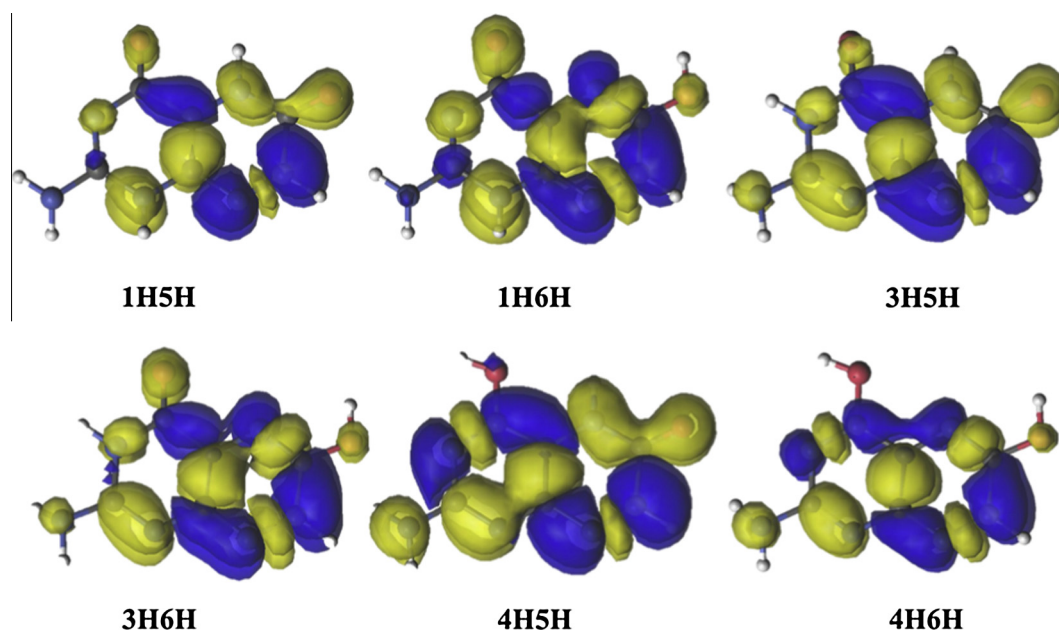
3H6H   **4H5H**   **4H6H**

Fig. 4. Differential electron density for the lowest-energy electronic transition in the isomers of xanthopterin computed at the ground-state optimised geometry. The electron promotion occurs upon light irradiation from yellow to blue regions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
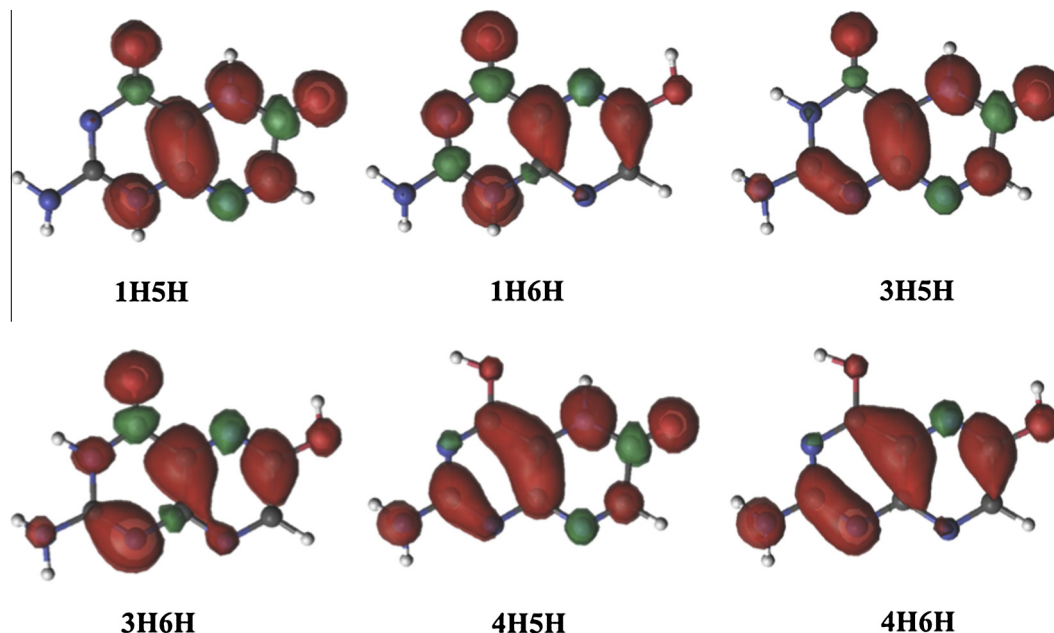
Fig. 5. Spin density for the cations of the isomers of xanthopterin computed at the ground-state equilibrium structure of the neutral systems.

delocalization of the unpaired electron extended to the NH_2 group (cf. Fig. 5), the effect of including the out-of-plane lone-pairs in the active space has been also tested for the six isomers. A decrease of the *VIP* values in the range 0.02–0.14 eV is obtained, although not changing the conclusions derived from the present data. The trend of the *VIP* results might be mainly explained by the extension of the delocalization of the produced unpaired electron over the π orbitals of the molecules (see Fig. 5). Hence, 4H5H and 3H5H present the lowest *VIP* and largest delocalization, whereas 1H6H shows the opposite behaviour.

Attachment energies *VAE* have similar trends as the *VIP* values. The magnitude of the tautomerism effect is, however, much more intense in the amino/imino tautomers. Hence, N_1-amino forms have *VAE* values 0.4–0.5 eV smaller than the N_1-imino structures. The reasons for that result can be found in the smaller relaxation of the molecular structure taking place in the 1H5H and 1H6H isomers along the evolution towards the equilibrium structure of the cation systems. Whereas the amino group at position C_2 of the N_1-amino isomers maintains the pyramidalization, it becomes completely planar in the other four isomers. As can be seen in Fig. 5, the protonation of N_1 instead of N_3 seems to prevent the delocalization of the unpaired electron over the NH_2 group and therefore the conjugation with the rest of the π system is not possible.

Regarding the electronic couplings H'^{ET} and H'^{CT} related to the magnitude of the π interaction in the homodimers, a certain dependence on the presence of the keto groups is found in average. Thus, larger H'^{ET} couplings are found for the lactam form at ring A than for the lactim tautomer (the energy differences are up to 0.4 eV, which corresponds to an energy splitting ΔE_{ET} of 0.7 eV between the excimer states). This is in agreement with previous findings reported for the excimer stabilization of homodimers of DNA nucleobases [37–40]. In contrast to the present computed H'^{ET} values, the mentioned effects seem to affect much less the CT and the approximate H'^{CT} results do not allow seeing any significant change caused by the molecular structure.

On the basis of the *VIP*, *VAE*, H'^{ET} and H'^{CT} results and the comparison for the six isomers, the electron donor, electron acceptor, energy transfer and charge transfer properties can be examined.

The 3H5H and 4H5H isomers (followed at close energies by 4H6H and 1H5H) are more easily ionised and therefore more prone to donate an electron to the environment (such as in the dye-sensitised solar cells). On the contrary, the regeneration of the neutral system would be more favourable in the N_1-amino isomers, which have the largest *VAE*. After light absorption, xanthopterin might facilitate, via excimer interactions, the transport of energy until an electron donation to another molecular system takes place and subsequently the produced hole might be transported via a similar excimer-like mechanism, which has been also proposed previously for DNA [33,41,42] and for triplet energy transfer processes that produce singlet oxygen from psoralen [32]. According to the present computed H'^{ET} values, the ET process is predicted to be enhanced in the lactam-lactam forms, i.e., 1H5H and 3H5H.

4. Conclusions

The CASPT2//CASSCF methodology has been used to analyse the molecular basis of the functions of xanthopterin as light-harvesting system in bio-organisms and in a dye-sensitised solar cell built by Plotkin et al. [8]. A systematic comparative analysis has been performed on the basis of the computations for six xanthopterin isomers of absorption and emission E_{VA}, E_{VE} and T_e energies, fluorescence τ_{rad} lifetimes, ionisation potentials *VIP*, electron attachment energies *VAE* and electronic couplings H'^{ET} and H'^{CT}.

The 3H5H isomer is predicted as the most stable in the gas phase and its higher stability is also estimated for polar environments. Moreover, a certain population probability might be expected for the N_1-imino isomers in the gas phase and for the B ring lactam isomers in polar solvents. The lactam–lactam forms 1H5H, 3H5H and 4H5H have the lowest-energy values for the absorption and emission energies. In particular, the 3H5H species is ascribed as the main responsible for the lowest-energy absorption band observed experimentally in solutions of xanthopterin [34]. Regarding the electron donor and acceptor properties and the efficiencies estimated for the ET and CT processes via π-stacking between homodimers, both 1H5H and 3H5H show more favourable characteristics than the other isomers for electron donation of the neutral form and electron attachment of the

produced cationic system and for energy and charge transport. Based on the overall theoretical CASPT2 results, 3H5H is predicted as the molecular structure having the most appropriate intrinsic features for solar energy harvesting of xanthopterin.

Acknowledgements

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