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Theoretical calculation of the maximum absorption wavelength for Cyanidin molecules with several methodologies

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ABSTRACT

Seven functionals, M06-L, M06, M06-2X, M06-HF, M11, PBE0 and B3LYP with two different basis set were used in the determination of the absorption spectrum in two chemical arrangements, Cyanidin (Cy) and Cyanidin-chloride (Cy-Cl). This second arrangement is studied trying to reproduce the ethanol/HCl environment of the experimental results. The main objective of this work is to find to find the influence of the electronic correlation and exchange in the absorption spectrum of Cy and Cy-Cl systems. The results of the calculated vertical excitation energies were affected by the Hartree–Fock exchange involved in the exchange–correlation functional. This can be clearly seen in the maximum absorption wavelength values found with the different methodologies applied, from which can be concluded that the best results are obtained with M06-L/6-31G(d) that predicts 547.93 nm followed by M06-L functional in combination with the 6-31G+(d,p) basis set with 544.3 nm. The experimental value is 547 nm. Also, a linear regression was performed comparing the calculated geometrical parameters with X-ray experimental data to define the best level of theory to reproduce with high precision the structural geometry, this is B3LYP/6-31+G(d,p).

1. Introduction

Flavonoids are constituted by a wide variety of molecules; anthocyanins represent the principal flavonoid group and are also considered natural dyes. They are responsible for the cyan shades ranging from salmon to dark blue in most flowers, fruits and leaves [1]. The basic structure of the anthocyanins is the anthocyanidins or aglycons, which consist of an aromatic ring (A) bonded to an heterocyclic ring (C) containing an oxygen atom, this ring is also bonded by a carbon–carbon bond to a third aromatic ring (B), Fig. 1(a). The distribution of the six most common anthocyanidins in fruits and vegetables is: Cyanidin 50%, Delphinidin 12%, Pelargonidin 12%, Peonidin 12%, Petunidin 7% and Malvidin 7% [2]. These have several advantages: availability, ease of synthesis or extraction, non-toxicicity, environmental safety and high biodegrability. Also, they have shown beneficial properties for human health, including antioxidant and antitumor activity [3], furthermore they have been broadly studied as photosensitizers for the dye sensitized solar cell (DSSC) [4] due to their visible-light harvest.

The charge-transfer process in DSSC involves several steps. The inciding photon is absorbed by the dye in its ground state; it is excited and injects an electron into the conduction band of the TiO_2 semiconductor; as a result the excited dye becomes oxidized. The injected electron travels through an external load and it is collected at the counter electrode, where it is then accepted by the redox couple present in the electrolyte. The cycle is completed with the reduction of the dye to its ground state [5]. An effective dye must have the energy level of its excited state inside the conduction band of the oxide semiconductor to carry out an effective electron transfer. In addition, its redox potential should be high enough to regenerate due to electron donation from the electrolyte. Furthermore, it must absorb light within the solar spectrum from the UV to the near IR range [6]. Therefore, the study of the absorption spectrum and optical properties of dyes is essential in this type of devices.

In recent years, time-dependent density functional theory (TD-DFT), an important approach to the calculation of excitation energies, has been extensively used to study the structure and absorption spectra of sensitizing dyes for DSSCs [7–11]. It is an

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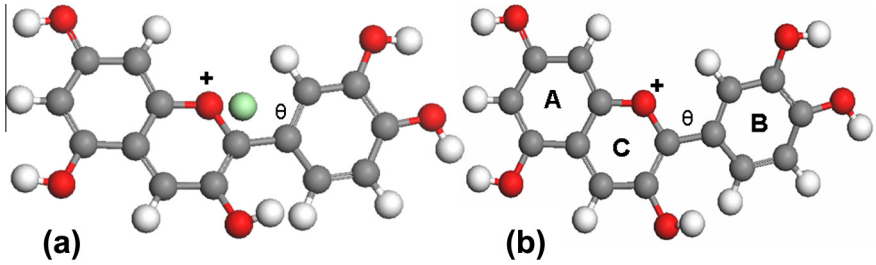

Fig. 1. Optimized geometry of Cyanidin-chloride (a) and Cyanidin (b).

important tool with low computational cost, based on the Kohn–Sham molecular orbital method, which gives a good molecular orbital description of the ground state electronic structure and the nature of the excitations. However, the TD-DFT transition energies are affected by the nature of the functional. The method achieves consistent values for the maximum absorption wavelength (λmax) and electronic transitions of dyes with different functionals; thus the functional proves crucial part to obtain high quality results.

Regarding functionals development, the local spin density functionals (LSDA) are considered the first generation of functionals, in which density functionals rely only on local densities, whereas the second generation of density functionals, is the generalized gradient approximation (GGA), in which functionals depend on the gradient of the electronic density as well as electronic density itself. The hybrid GGA functionals are determinated on the Hartree–Fock (HF) exchange and on the electronic density and its gradient. In the third generation of functionals, kinetic energy densities are included in the functional form; these functionals are called meta-GGAs. Hybrid meta-GGA functionals depend on the Hartree–Fock exchange, electronic density and its gradient as well as the kinetic energy density [12]. The functionals defined in the methodologies for this work were selected considering the notable progress in the development and validation of density functionals and considering the precision of a DFT calculation rests on upon the exchange–correlation (XC) quality.

In this work, we evaluate seven functionals combined with two Pople type basis set widely used to calculate organic dyes, in order to compare their performance predicting maximum wavelength of 2-(3,4 dihydroxyphenyl) chromenylium- 3,5,7-triol chloride (*Cyanidine chloride or Cy-Cl*) and 2-(3,4 dihydroxyphenyl) chromenylium- 3,5,7-triol (*Cyanidine or Cy*) dyes with experimental data, in an attempt to find the influence of the amount of electronic exchange of these functionals over this important property of common dyes used in DSSC. The Cy-Cl molecule calculation was performed in order to reproduce the ethanol/HCl environment. The methodology validation was accompanied with a linear regression, without hydrogen atoms, of the calculated geometrical parameters compared with X-ray data [13]. Knowledge obtained from this study will aids in developing future calculations of the main principal properties of interest for this kind of molecules when used as photosensitizers.

2. Computational details

A PM3 semiempirical conformational analysis was performed for Cyanidin (Cy) and Cyanidin chloride (Cy-Cl) by using the Hyperchem 8.0 program [14] in order to find the most stable conformer considering the torsional angles. All the DFT computational calculations were carried out with the Gaussian 09W package [15]. Geometry optimization in solvent at the ground and excited states was performed. The force constants and vibrational frequencies calculations have also been carried out to check imaginary eigenvalues and to confirm for true minima structure.

The functionals used to carry out this study are: Perdew, Burkeand Ernzerhof, PBE0 [16] and Becke Three Parameter Lee, Yang, and Parr, B3LYP [17], both corresponding to the hybrid GGA functionals, which have shown good agreement with experimental values in organic dyes [18]; the M06 suite developed by Truhlar and coworkers at University of Minnesota, which consists of meta generalized gradient approximations (meta-GGAs) M06-L [19] and global-hybrid meta-GGAs, M06 and M06-2X [20], M06-HF [21] and M11 [22], functionals with different percentage of Hartree–Fock. All these functionals were combined with two Pople type basis sets: 6-31G(d) [23] and 6-31+G(d,p) [24].

The absorption spectra were calculated by solving the time-dependent density functional theory (TD-DFT) equations [25,26]. The equations were solved for 20 excited states, where the computational studies were performed in presence Ethanol as solvent, using the IEFPCM (integral equation formalism PCM) method coupled to UAKS radii. In the PCM (Polarisable Continuum Model) scheme [27,28], the solute molecule is placed in a shape-adapted cavity surrounded by the implicit solvent described as a continuum dielectric, which is characterized by its dielectric constant [29]. The IEF method originally developed by

Table 1
Correlation coefficients of bond distances for various methods used in geometry optimization of Cy and CyCl.

Compound	Functional	R^2
Cy	B3LYP/6-31G(d)	0.9285
	B3LYP/6-31+G(d,p)	0.9330
	M06/6-31G(d)	0.9147
	M06/6-31+G(d,p)	0.9176
	M06-2X/6-31G(d)	0.9191
	M06-2X/6-31+G(d,p)	0.9116
	M06HF/6-31G(d)	0.8913
	M06HF/6-31+G(d,p)	0.8813
	M06L/6-31G(d)	0.9139
	M06L/6-31+G(d,p)	0.9196
	M11/6-31G(d)	0.9227
	M11/6-31+G(d,p)	0.9146
	PBE0/6-31G(d)	0.9017
	PBE0/6-31+G(d,p)	0.9049
CyCl	B3LYP/6-31G(d)	0.9178
	B3LYP/6-31+G(d,p)	0.9202
	M06/6-31G(d)	0.8916
	M06/6-31+G(d,p)	0.8940
	M06-2X/6-31G(d)	0.9056
	M06-2X/6-31+G(d,p)	0.8880
	M06HF/6-31G(d)	0.8305
	M06HF/6-31+G(d,p)	0.8488
	M06L/6-31G(d)	0.9017
	M06L/6-31+G(d,p)	0.9061
	M11/6-31G(d)	0.8941
	M11/6-31+G(d,p)	0.8888
	PBE0/6-31G(d)	0.8940
	PBE0/6-31+G(d,p)	0.8944