

Experimental and computational study of electronic, electrochemical and thermal properties of quinoline phosphate

Takoua Ben Issa ^{a, b}, Chedia Ben Ali Hassine ^c, Houcine Ghalla ^{d, *}, Houcine Barhoumi ^c, Latifa Benhamada ^a

^a Energy and Materials Laboratory, Higher School of Science and Technology Hammam Sousse, University of Sousse, Sousse, 4054, Tunisia

^b Faculty of Sciences, University of Monastir, Monastir, 5000, Tunisia

^c Laboratory of Interfaces and Advanced Materials (LIMA), University of Monastir, 5000, Tunisia

^d Quantum Physics Laboratory, Faculty of Sciences, University of Monastir, Monastir, 5000, Tunisia

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ABSTRACT

In this work, the electronic behavior, charge transfer, non linear optical (NLO) properties, and thermal stability of the quinoline phosphate (QP) have been investigated. The experimental UV–Vis spectrum has been recorded in the range of 200–800 nm. Additionally, the absorption spectrum was reproduced by time-dependent density functional theory (TD-DFT) method with B3LYP functional and with empirical dispersion corrections D3BJ in combination with the 6–311+G(d,p) basis set. The electronic properties such as HOMO-LUMO energy gap and chemical reactivity have been calculated. The electrochemical characterization of the title compound is investigated using cyclic voltammetry and impedance spectroscopy methods. Finally, the thermal stability of the QP is discussed in term of differential scanning calorimetry (DSC) measurement, which showed that QP compound is thermally stable up to 150 °C.

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1. Introduction

Recently extended scientific research is focused on the investigation of charge transfer properties in hydrogen-bonded compounds. This field of research has received considerable attention not only for understanding numerous biophysical processes in the biological systems, but also because their applications as the electrolyte for fuel and electrolysis cells [1,2]. In particular, organic phosphate complexes attract more and more the attention of many scientists all over the world. These materials have been the subject of various structural and theoretical studies regarding to their applications in different field of the sciences [3–7]. They were potentially good candidates for NLO applications [8], photocatalysts [9,10], as well as biology [11–13] and medicinal uses [14–16]. The originality of these results depends not only to the organic or inorganic parts itself, but also to the morphology and the structure of the final compound. Moreover, the choice of the organic molecule involved in the structure of the hybrid compound is very important because it influences intensively the final result.

The quinoline is a good candidate regarding to its ability as a good established feature in a variety of naturally occurring and medicinally active compounds [17]. Concerning to its easy process and its potential applications, quinoline is one of the most studied heterocyclic compounds. The quinoline rings feature in a variety of naturally occurring and medicinally active compounds. These compounds were used as a treatment for parasitic infections. They are useful as antimicrobial [18–20], antitubercular [21,22], anti-malarial [23–25], anti-allergic [26] and antiasthmatic activity [27].

In a recent study, we have reported the X-ray diffraction and theoretical molecular structure, Hirshfeld surfaces, topological analyses and spectroscopic vibrational assignment of QP [28]. Fig. 1 shows that in the crystal packing of QP inorganic and organic components are connected through hydrogen bonding and $\pi \cdots \pi$ interactions. Additionally, the main important role in the process of self-assembly of QP salt is played by strong self-association via O–H \cdots O (N) hydrogen bonding and also $\pi \cdots \pi$ interactions. These interactions have been proved by the topological AIM analysis and Hirshfeld surface analysis.

From the literature, the electronic, electrochemical, and thermal properties of the QP are not yet reported. In the first section, the experimental UV–Vis spectrum absorption has been recorded

* Corresponding author.

E-mail address: houcineghalla@yahoo.fr (H. Ghalla).

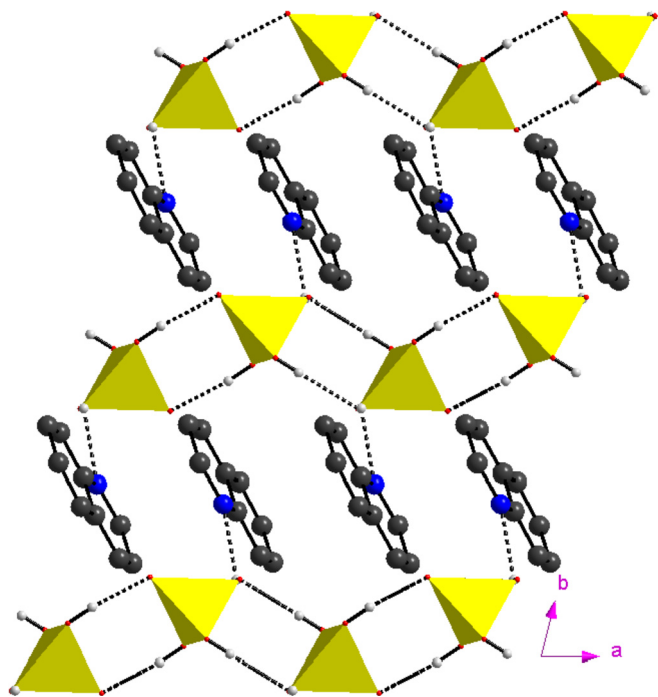


Fig. 1. Crystal packing of QP complex.

within the range of wavenumbers of 200–800 nm. TD-DFT calculations have been performed in order to discuss the electronic transitions within the compound. The NBO analysis has been carried out to investigate the stability of the molecule and charge delocalization. In addition, the NLO properties of the QP compound have been discussed and compared to those found experimentally for salts of quinoline. In the second section, the dielectric behavior of QP was investigated through cyclic voltammetry and impedance spectroscopy methods. The following section undertakes the thermal behavior of the considered compound in term of DSC.

2. Experimental details

The studied compound has been prepared by the slow evaporation method, as reported previously [28]. At room temperature, the UV–Vis spectrum of QP was performed by the use of Perkin Elmer Lambda 950 spectrometer in the range between 200 and 800 nm. The reference material used for this measurement was ethanol ($[QP] = 5.10^{-5}$ mol/L).

Electrochemical measurements were performed using a traditional three-electrode cell. This latter was containing a platinum wire as a counter electrode and glassy carbon electrode (GCE) as working electrodes with a geometric area of 0.07 cm^2 . The Ag/AgCl in saturated KCl (Ag/AgCl/(sat.KCl)) was used as a reference electrode. For this task, 2 mg of QP was dispersed in 1 mL of N, N-dimethylformamid. Then, $5 \mu\text{L}$ of the QP solution was dropped directly on the surface of a clean glassy carbon electrode GCE surface and dried at room temperature to form a QP modified GCE. The electrochemical experiments were carried out using an Autolab PGSTAT 320 N potentiostat for impedance spectroscopy spectra measurements controlled by computer with software (NOVA 1.5) for data analysis.

DSC measurement was performed on heating samples from 30° to 350°C on a SETARAM apparatus (model DSC 92) at a heating rate of $5^\circ \text{C}/\text{min}$.

3. Theoretical details

Starting from the crystal structure [28], the QP was optimized using ORCA 3.0 program [29] and applying the DFT method using global hybrid Generalized Gradient Approximation (GGA) functional B3LYP coupled to the empirical Becke and Johnson damping dispersion corrections D3BJ [30–32] in combination with the 6-311++G(d,p) basis set. The B3LYP-D3BJ was selected as a widely applicable method that proved to describe weak intermolecular interactions, more accurately and reliably than traditional DFT methods [33–40]. The optimization was performed with resolution of the identity approximation along with chain of spheres exchange method (RIJCOSX) [41]. The vibrational frequencies have been calculated at the same level of theory, and the absence of imaginary frequencies proves that the optimized geometry is a minimum on its potential energy surface. The optimized structure along with the atom numbering is given in Fig. 2.

TD-DFT approach [42,43], at the same level of theory in the implicit solvation model COSMO [44], was applied to simulate the UV–Vis spectrum and electronic properties, such as absorption wavelength, oscillator strength and HOMO-LUMO energy gap. Here ethanol ($\epsilon = 24.3$) was taken as implicit solvent, as it is used during the experiment. It is worthy to note that, recent research proves that TD-DFT theory has a potential role in the examination of the dynamic and static properties of the complexes within their excited states [42]. It allows for the best correlation between accuracy and computational cost. Moreover, the contribution percentages of the investigated electronic transitions have been simulated by GaussSum-3.0.1 program [45]. Finally, the optimized geometry was used to perform the NBO analysis and to determine the NLO properties with the help of Gaussian 09 package [46].

4. Results and discussion

4.1. Electronic behavior

Experimental and predicted UV–Vis spectra of QP are shown in Fig. 3. A good correlation is observed between the calculated and the theoretical spectra. Experimentally, the absorption takes place in a weak zone between 250 nm and 350 nm. Furthermore, the experimental absorption maximum values have been localized nearly at 189 and 208 nm. Consequently, we can attribute these bands to the aromatic part of our compound (the quinoline sheets). These observations are similar for other studied on chromophores

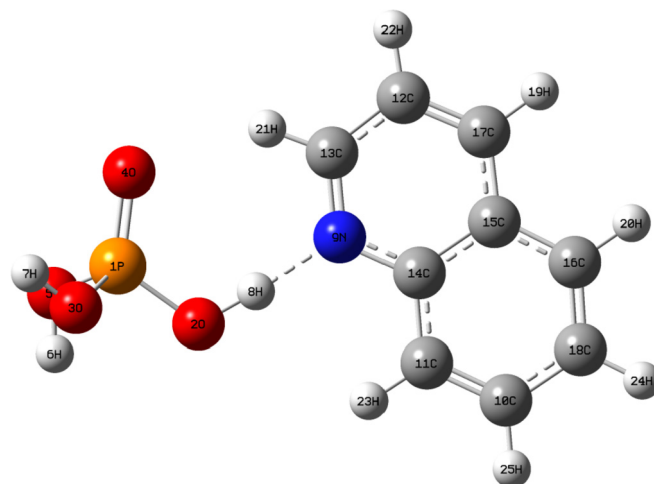


Fig. 2. Optimized molecular structure of QP optimized at B3LYP-D3BJ/6-311++G(d,p) level of theory.

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