



Crystal structure and theoretical studies on quinoline phosphate



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ABSTRACT

The crystal structure of (C₉H₇N) H₃PO₄ (QP) was determined from single crystals obtained by slow evaporation methods (space group P1; a = 7.5508(3) Å, b = 7.9705(3) Å, c = 8.6849(3) Å; α = 77.3725(18)°, β = 82.6225(19)°, γ = 74.9829(19)°). The crystal structure of QP is built up from infinite hydrogen bonding inorganic chains of (H₃PO₄)_n lay parallel to the an axis, which are also connected to the quinoline rings through hydrogen bonds in a 3D arrangement. The structure was examined through atoms in molecules (AIM) topological and Hirshfeld surface (HS) analyses and its molecular structure optimized by theoretical density functional (DFT) calculations. The QP observed IR absorptions between 4000 and 400 cm⁻¹ were assigned on the basis of the calculated theoretical vibrational modes.

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1. Introduction

In the last two decades hybrid materials has received a growing interest for its possible applications in different science fields [1–3]. Inorganic entities can be self-assembled into low dimensional crystals in which they form zero-(0-D) [4] one-(1-D) [5] and two-(2-D) [6] networks depending on the organic counter-ions. The compounds containing phosphates are among the most interesting crystalline systems, being the subject of a large amount of studies for their possible properties [7]. Materials such as “pillared layer” materials and three-dimensional frameworks are formed involving organophosphates ligands that promote the formation of alternating organic and inorganic layers [8]. The whole structure of these compounds depends on the morphologies and length of organophosphates, but also the chemical identity of the organic groups has a deep influence [9]. Different geometries have been obtained involving [HPO₄]²⁻ and [H₂PO₄]⁻, such as ribbons [10], chains [11], clusters [12], two-dimensional [13] and three-dimensional networks [14]. The presented study reports how obtaining single crystal of QP useful for being recorded by single X-ray diffraction investigation, its crystal structure, AIM topological HS analyses, molecular electrostatic

potential (MEP) surface and vibrational analysis. The compound was also studied by DFT that provided the correct assignment of the vibrational bands. Here, conscientious attention has been devoted to study the intermolecular O–H⋯N and O–H⋯O hydrogen bonding interactions through X-ray diffraction, AIM [15] and HS analyses and vibrational frequencies. CCDC 1551101 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

2. Experimental

2.1. Preparation

By slow evaporation single crystals of the studied compound were obtained from a solution of quinoline [Aldrich, Purity, ≥98% (NT)] and phosphoric acid (Aldrich, 40 wt% in H₂O, 99.95%) as obtained from commercial sources without further purification. A solution of quinoline (0.24 mol) in 20 mL of ethanol was added to a solution of phosphoric acid also in ethanol. The resulting solution was filtered through paper and left at room temperature. After several days, transparent and good single crystals were produced, which were filtered and air dried.

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2.2. Structure determination

Structural analysis of the QP was carried out at 100(2) K by an X-ray diffractometer BRUKER D8 VENTURE using Cu ($K\alpha$) ($\lambda = 1.54060$ Å) radiation. Table 1 shows the details of the crystal structure and its determination. All non-hydrogen atoms were refined anisotropically (Olex2) [16] by full matrix least squares on F^2 . All H atoms were positioned geometrically and refined with successive difference Fourier maps with using the SHELXL-97 program [17], fixing the bond length at 1.103 Å for O2–H8 group. R decreased to 4.87% ($R_w = 12.30\%$) in the final least-squares refinement of atomic parameters with isotropic thermal factors of the H atoms. Moreover, the drawings were made with Diamond package [18].

2.3. FT-IR spectrum measurement

The FT-IR spectrum of QP was recorded as a KBr pellet at room temperature using Bruker Vertex-70-FT-IR from 4000 to 400 cm^{-1} and with a resolution of ± 2 cm^{-1} .

3. Computational details

DFT-B3LYP method with 6–311++G(d,p) basis set were used to perform the quantum chemical calculations using the Gaussian 09 program [19] and visualized in GaussView program [20]. At the local true minima on the potential energy surface, the optimized geometry of the title compound was verified to be localized, as revealed by the lack of imaginary frequencies. The harmonic vibrational frequencies are scaled by an appropriate factor in order to assure a comparison with the experimental data. VEDA4 program [21] was used to assign the vibrational modes on the basis of Total Energy Distribution (TED) analysis. A topological analysis was performed using AIM2000 package [22], in particular, to characterize the intermolecular hydrogen bonds between the organic and the mineral fragments. Moreover, the intermolecular interactions of the crystal structure of the QP molecule were quantified using HS analysis and fingerprint plots.

Table 1
Crystal and refinement data obtained for QP compound.

Molecular formula	$\text{C}_9\text{NO}_4\text{H}_{10}\text{P}$
Formula weight	227.15 g/mol
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimension	$a = 7.5508(3)$ Å $b = 7.9705(3)$ Å $c = 8.6849(3)$ Å $\alpha = 77.3725(18)^\circ$ $\beta = 82.6225(19)^\circ$ $\gamma = 74.9829(19)^\circ$
Volume (Å ³)	491.20(3)
Z	2
T (K)	100(2)
Calculated density (g/cm ³)	1.536
Absorption coefficient (mm ⁻¹)	2.477
F(000)	236.0
Color, habit	colorless, prismatic
Crystal size (mm)	
θ range for data collection (°)	5.23–77.46
Index ranges	$-9 \leq h \leq 9$; $-9 \leq k \leq 9$; $-10 \leq l \leq 10$
Reflections collected/unique	18341/1975
Data/parameters/restraints	1975/176/0
Goodness-of-fit on F ²	1.0951
Final R indices [$I > 2\sigma(I)$]	0.0488
Largest diffraction peak and hole ($e/\text{Å}^3$)	0.5629 and -0.6421

4. Results and discussion

4.1. Molecular structure

The QP single crystal belongs to the $P\bar{1}$ space group of triclinic system with two formula units in the unit cell ($Z = 2$). Fig. S1 shows that the asymmetric unit of QP was formed by one molecule of quinoline and one phosphoric entity H_3PO_4 . The molecular structure of the QP molecule was optimized using DFT-B3LYP method with 6–311++G(d,p) as basis set. The optimized geometry of the QP along with labels of atoms is shown in Fig. 1. The conditions for the data collection and the structure refinement parameters are given in Table 1. Experimental X-ray crystal data and theoretical structural parameters of the QP are listed in Table 2. It is obvious to show that the majority of the experimental values of bond lengths are slightly shorter than the optimized ones. This discrepancy may be attributed to the hydrogen bonding interactions in the solid phase that are not taken into account in the calculations which are performed in the gas phase. Moreover, the calculation has been made for an isolated molecule without taking in consideration the interactions with the neighboring entities. Consequently, we admit that the cluster approach will be sufficient to investigate the intermolecular interactions between different entities of QP. A view of the structure along the a axis is reported in Fig. 2. The atomic arrangement of the QP complex was described by a three-dimensional network formed by an infinite chain $(\text{H}_3\text{PO}_4)_n$ propagating along the a -axis, interconnecting to the quinoline entities. The mineral skeleton of this compound is formed by H_3PO_4 groups which are interconnected via $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bond leading to the formation of infinite chains of phosphates $(\text{H}_3\text{PO}_4)_n$ in the (b, c) plane.

Fig. 3 illustrates the intermolecular hydrogen bond interactions $\text{O} \cdots \text{H} \cdots \text{O}$ between the phosphate entities, which constitute an infinite chain $(\text{H}_3\text{PO}_4)_n$ propagating along the a -axis. In addition, P–O distances vary in the range [1.497(2)–1.573(2) Å] (Table 2). The review of these distances reveals that the distance P–O4 [1.497(2) Å] is the shortest, this is due to the location of a protons on oxygen atoms O2, O3 and O5 of the H_3PO_4 molecule. The average values of P–O distances and O–P–O angles are 1.534(3) Å and 109.39(15)°. They are in good agreement with that generally observed in monophosphate group which is with respect to those found in anions of similar salts [23]. The calculated average values

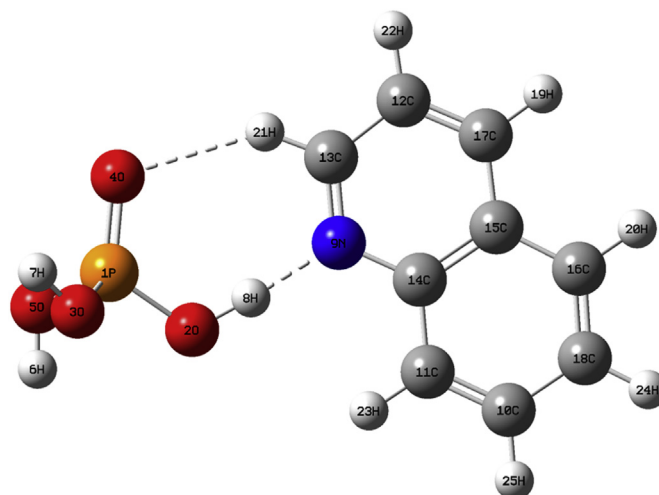


Fig. 1. Optimized molecular structure of QP optimized at DFT-B3LYP/6–311++G(d,p) level of theory.

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