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Supramolecular Assemblies Driven by N-H…O and O-H…O Hydrogen Bonding Interactions: Experimental and Theoretical Investigation into the Supramolecular Architectures of Dihydropyrimidin-2(1H)-ones †

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Abstract

In this paper, quantum chemical calculations at the DFT/6-311G (d,p) level of theory have been carried out to study the supramolecular structure of dihydropyrimidin-2(1H)-ones. Theoretical studies such as Hirshfeld surface analysis, MEPS (molecular electrostatic potential surface), and HOMO-LUMO calculation were also carried out to obtain the energy gap and to determine the kinetic stability and chemical reactivity. The crystal structure of dihydropyrimidin-2(1H)-ones shows the present of N-H…O and O-H…O hydrogen bonding interactions. The N-H…O bond lengths are 2.102 Å and 2.037 Å, respectively. The theoretical hydrogen bonding interactions were also compared with the available experimental data and found to be closely related.

Keywords: supramolecular; DFT; crystal structure; hydrogen bonding; Hirshfeld

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1. Introduction

In chemistry and materials science, using molecules having supramolecular synthons as building blocks to create network solid and functional materials via non-covalent interactions has become importance [1–4]. It is possible to achieve intriguing chemical and physical properties of the constructed networks by integrating various capabilities into the building elements [5]. One of the most common methods used in the creation of supramolecular network solids is hydrogen bonding. Because of its well defined, repeated, and transferable directionality qualities, hydrogen bonding has been referred to as "the master key interactions in supramolecular chemistry [6–10].

To achieve the desired molecular ordering in the crystalline state, it is very crucial to comprehend the supramolecular interaction of organic crystals with different secondary bonds, such as hydrogen bonds, π–π interactions and other non-covalent interactions [2–4]. Organic crystals frequently consist of complex molecules with numerous substituents and a relative large size, which can lead to the creation of complex secondary bonds, in contrast to inorganic crystals with primary simple constituent atomic units.

Hence, the main purpose of this study was to investigate the ability of dihydropyrimidin-2(1H)-ones to form supramolecular structure using different kind of molecular interactions. Moreover, dihydropyrimidin-2(1H)-ones was one of the most important heterocyclic compounds, which exhibits significant biological activities and widely studied [11,12]. This study focus on dihydropyrimidin-2(1H)-ones, specifically how these molecules with multiple hydrogen bonding sites interact within crystals to establish a synthon hierarchy.

2. Results and Discussion

The optimized geometrical structure of DHP1, DHP2 and DHP3 are shown in Figure 1. The geometry of DHP1 was optimized without any water molecule, whereas the structure of DHP2 and DHP3 were optimized together with water molecules. The optimization was carried out to compare the theoretical hydrogen bonding interactions present inside the crystal lattice with an experimental data obtained from single crystal. As shown in the Figure 1, theoretical hydrogen bonding interactions of DHP2 and DHP3 are 1.691 Å and 1.687 Å, respectively. The theoretical hydrogen bonding interactions were also compared with the available data of some of the compound available in the Cambridge structure data base (CCDC number 1455902) is 1.825 Å (DHP2) Figure 4, and found to be closely related. However, some deviation between experimental data and DFT were observed [13]. This results can be attributed that the experimental data geometrical (single crystal x-ray crystallography) data done in solid state where the intermolecular interactions became prominent, whereas the theoretical data where the optimization were carried out in gaseous state in which intermolecular interactions are absent and moreover, its structure is more extended compared to single crystal x-ray data.

The molecular electrostatic potential surfaces of DHP1, DHP2 and DHP3 are shown in Figure 2. The green colour indicates the zero potential, blue colours represent the positive potential of the compound and the red colour indicates the negative potential (Figure 2). The red colour regions are due to high electron density and correspond to a strong attraction, whereas the blue colour region corresponds to low electron density with weak interaction. Similarly, the molecular electrostatic potential of DHP1, DHP2 and DHP3, the negative regions are mainly localized over the carbonyl oxygen atom, whereas the maximum positive regions are localized over the oxygen of the water molecule. Counter plots of selected molecular orbitals of DHP1, DHP2 and DHP3 and the HOMO-LUMO energy gap are shown in Figure 3. The energy gap (ΔE) of DHP1, DHP2 and DHP3 are 4.853 eV, 4.349 eV and 4.271 eV, respectively. Hence, DHP1 has higher energy gap compared to DHP2 and DHP3, it indicates that DHP1 has high stability and low chemical reactivity, whereas DHP3 with a small energy gap exhibits high chemical reactivity and less stable.

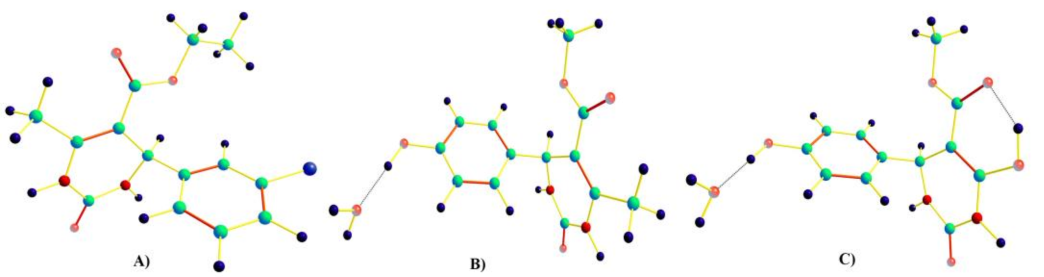

Figure 1. The optimized geometrical structure; (**A**) DHP1; (**B**) DHP2; (**C**) DHP3.

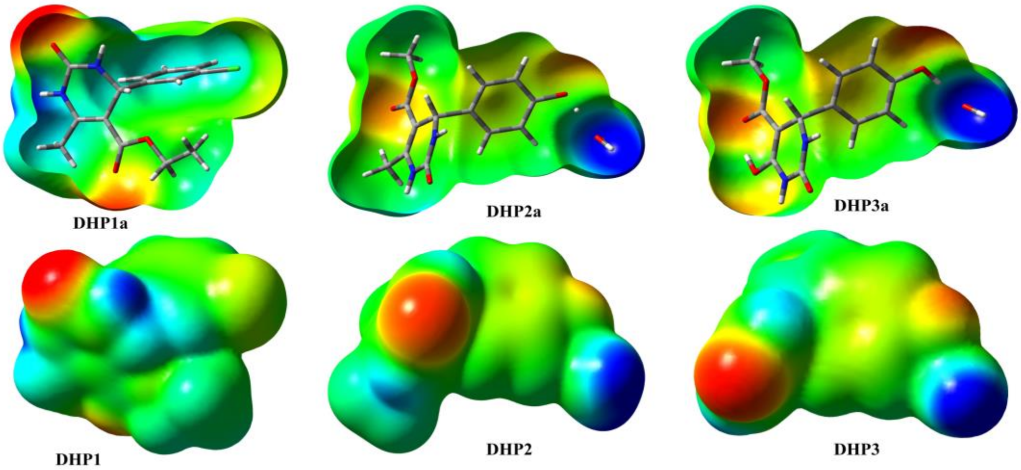

Figure 2. Molecular electrostatic potential maps of DHP1, DHP2 and DHP3 in the neutral state, and in the anion state. The different color gradient represents the electrostatic potential; the red color region represents negative potential, whereas the blue color represents positive potential.

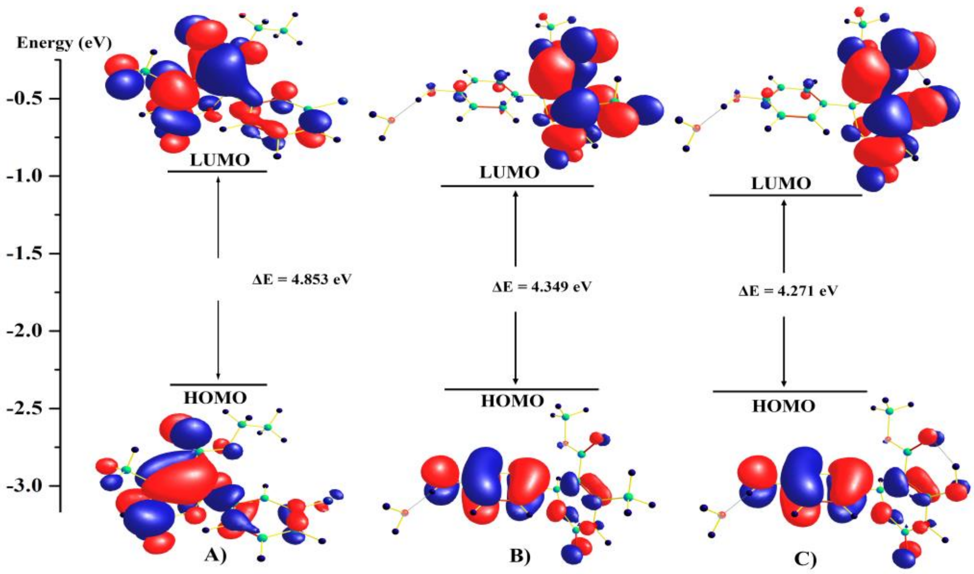

Figure 3. HOMO-LUMO plots of DHP1, DHP2 and DHP3 and their energy gaps.

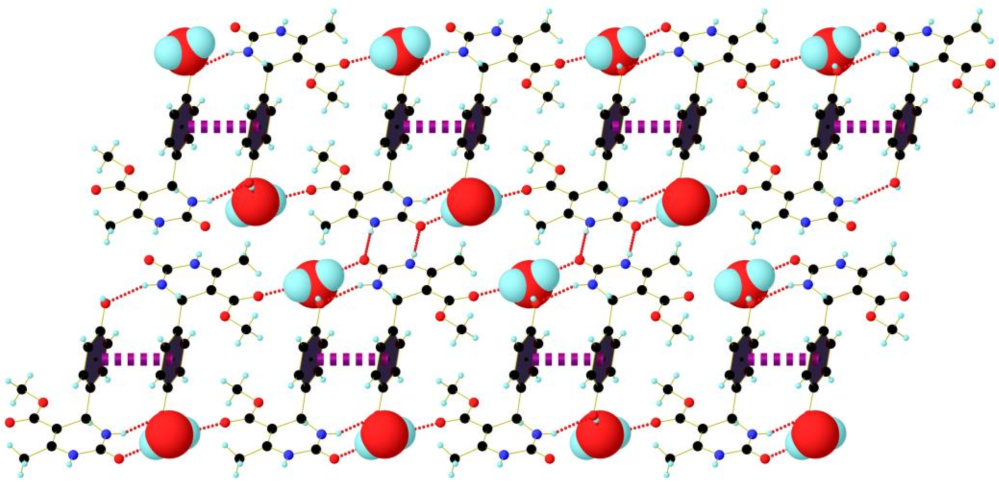

Figure 4. Crystal structure of DHP2 showing supramolecular interaction formed by hydrogen bonding interactions.

3. Experimental

3.1. Computational Studies

Density functional theory (DFT) has been used in geometric optimizations to ascertain minimum energy configurations and stable molecular geometries of DHP1, DHP2 and DHP3. The geometrical optimization was carried out using B3LYP level of theory along with 6-311G (d,p) basis set. The calculation on all the compounds have been performed successfully using Gaussian 09 software.

3.2. CSD Search

We have also explored the CSD in order to find some experimental support for the non-covalent interactions discussed above (CCDC number 1455902). Interestingly we have found the crystal structures of DHP2 where dihydropyrimidin-2(1H)-ones derivatives is establishing simultaneous hydrogen bonding and π–π interactions.

4. Conclusions

In this study, the structure of three compound of dihydropyrimidin-2(1H)-ones (DHP1, DHP2 and DHP3) was successfully optimized using Density functional theory (DFT). It was found that the theoretical hydrogen bonding interactions were also compared with the experimental data and found to be closely related. The molecular electrostatic potential surfaces of DHP1, DHP2 and DHP3 shows that the negative regions are mainly localized over the carbonyl oxygen atom, whereas the maximum positive regions are localized over the oxygen of the water molecule. Similarly, the energy gap (ΔE) of DHP1, DHP2 and DHP3 were also calculated and found that, DHP1 has higher energy gap compared to DHP2 and DHP3, it indicates that DHP1 has high stability and low chemical reactivity, whereas DHP3 with a small energy gap exhibits high chemical reactivity and less stable.

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Conflicts of Interest: The authors declare no conflicts of interest.

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