



DFT studies of 5-fluorouracil tautomers on a silicon graphene nanosheet



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ABSTRACT

We have performed density functional theory (DFT) calculations to evaluate properties for tautomers of 5-fluorouracil (FU), as an anticancer medicine, in the free form and in the hybridized form with a representative silicon graphene (SiG) nanosheet. All the structures have been fully relaxed to obtain the optimized geometries and energy parameters. The results indicated that the total and binding energies have good clues to determine the properties of tautomers and hybrid structures. Moreover, quadrupole coupling constants (C_Q) have been evaluated for the optimized structures to run an atomic level characterization of the investigated structures. The obtained results indicated that the properties for fluorine atoms are characteristically changed through tautomerism and hybridization processes.

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1. Introduction

Since the early days of nanotechnology opening, considerable efforts have been dedicated to show the significance of the novel technology in the fields of life sciences [1,2]. Among which, the planar nanostructures have been viewed as proper surfaces to keep and carry the biological molecules [3,4]. Tautomerism, which is the process of changing hydrogen atoms positions between oxygen and nitrogen atoms, is commonly occurring for the biological molecules yielding new properties for the resulted tautomeric structures [5]. Since detection of stabilities and properties of tautomeric structures is important for characterizing the biological systems, numerous investigations have been performed to achieve the purpose [6–10]. Quantum computations, which exactly show atomic and molecular properties, are used among proper techniques to investigate the tautomeric structures [11,12].

Within this research, we have employed the computational techniques to detect the optimized structures and properties for 5-fluorouracil tautomers on a representative model of silicon graphene (SiG) nanosheet (Fig. 1). Possibilities of existence for non-carbon nanostructures in additions to carbon ones have been approved by several works, in which the silicon based nanostructures could be expected as harmless materials for biological systems [13,14]. 5-Fluorouracil, as an anticarcinogenic drug, has been commonly used in cancer therapies for a long time with unwanted side effects for its users [15]. It is a fluorinated derivative of uracil, the characteristic RNA nucleobase, with tautomerism process possibility in the pyrimidine heterocyclic ring [16]. Although the stoichiometry of tautomeric structures is similar to the original one, but biological mutations could be happened by the existence of tautomers [17]. Electronic and structural properties, which define the behavior

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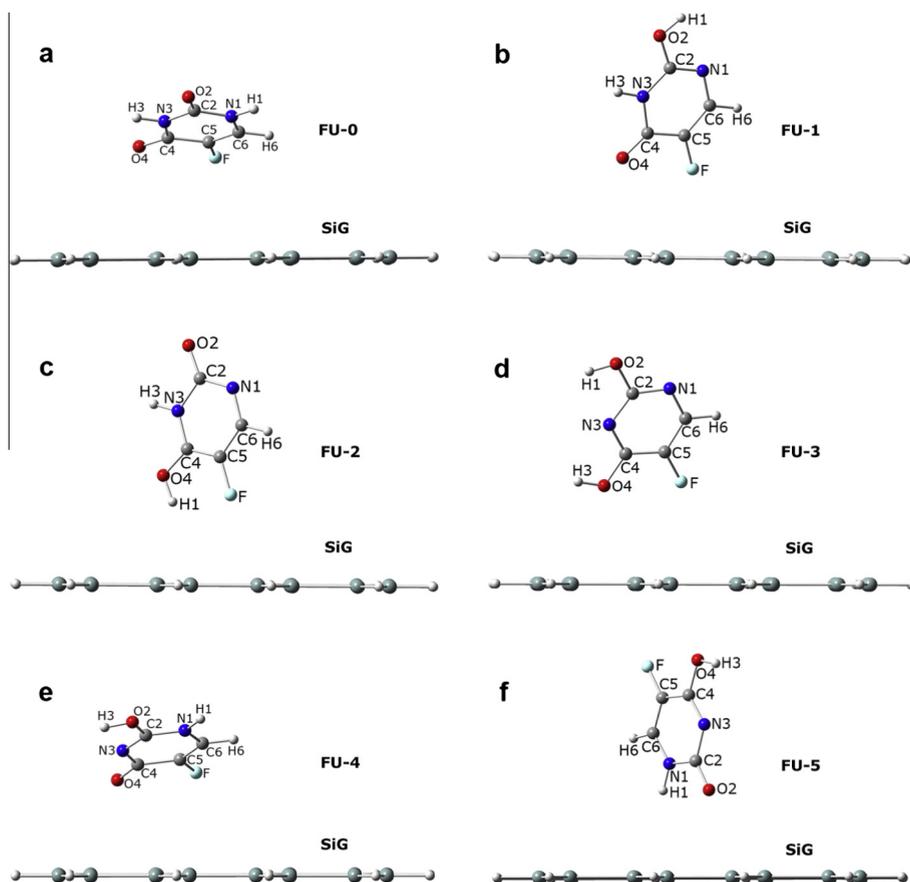


Fig. 1. The relaxed FU structures on the SiG nanosheet surface.

of matters, are changed for the tautomers in comparison with the original molecules; therefore, detection of behavioral discrepancies is an important task for the possible tautomeric structures [18]. Moreover, the orders of stabilities for tautomers could be changed in different environments, which are important to be investigated [19–22]. The major question of this work is to investigate the influence of silicon graphene nanosheet, as a representative nanostructure, on the optimized structures and properties of 5-fluorouracil tautomers. To this aim, molecular and atomic properties (Tables 1 and 2) have been computationally evaluated for the investigated systems (Fig. 1).

2. Computational details

We have performed density functional theory (DFT) calculations to optimize the structural models of 5-fluorouracil (FU) tautomers and the representative silicon graphene nanosheet (SiG) (Fig. 1). A molecular model for SiG is created with the stoichiometry of $\text{Si}_{36}\text{H}_{16}$ and six models of FU are created as one original structure and five tautomers all with the

Table 1
Molecular properties^a.

Model	ΔE_T (eV)	E_B (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	D_M (Debye)
FU-0	0; 0 [0.001]	-77.108; -77.108 [-0.083]	-6.786; -6.789 [-4.412]	-1.378; -1.388 [-3.801]	3.903; 3.930 [1.601]
FU-1	0.464; 0.464 [0.001]	-76.645; -76.644 [-0.098]	-6.494; -6.497 [-4.309]	-1.189; -1.200 [-3.705]	4.088; 4.150 [4.996]
FU-2	0.950; 0.955 [0.006]	-76.159; -76.153 [-0.172]	-6.360; -6.346 [-4.559]	-1.585; -1.577 [-3.948]	5.805; 5.958 [6.572]
FU-3	0.673; 0.674 [0.001]	-76.435; -76.434 [-0.082]	-6.718; -6.718 [-4.433]	-1.099; -1.097 [-3.825]	2.530; 2.564 [1.338]
FU-4	0.832; 0.833 [0.003]	-76.277; -76.275 [-0.120]	-6.617; -6.609 [-4.330]	-0.870; -0.880 [-3.726]	6.658; 6.733 [4.461]
FU-5	0.616; 0.617 [0.002]	-76.493; -76.491 [-0.128]	-6.518; -6.510 [-4.398]	-1.506; -1.527 [-3.785]	3.475; 3.543 [1.587]

^a The values are delta total energies (ΔE_T), binding energies (E_B), energies of the highest occupied molecular orbital (E_{HOMO}), energies of the lowest unoccupied molecular orbital (E_{LUMO}), and dipole moments (D_M). For ΔE_T , the values of brackets are the differences between the values of free and separated FU structures. For E_B , the values of brackets are the interaction energies of FU structures with SiG nanosheets whereas the other two values are the magnitudes of released energies during the formation of FU structures from the constructing atoms in free and separated forms. The values of E_{HOMO} , E_{LUMO} , and D_M in each row are for free and separated FU structures and [hybrid] forms. See Fig. 1 for the models.

Table 2
Atomic properties^a.

Atom	FU-0	FU-1	FU-2	FU-3	FU-4	FU-5
F	64,234; 64,403 [63,845]	63,246; 63,467 [63,001]	63,167; 63,405 [63,326]	63,750; 63,901 [63,421]	62,905; 63,041 [62,553]	64,648; 64,665 [64,653]
O2	8243; 8245 [8253]	9422; 9421 [9418]	8829; 8836 [8802]	9362; 9359 [9357]	9363; 9376 [9368]	8790; 8880 [8664]
O4	9434; 9458 [9393]	9024; 9071 [8925]	9311; 9464 [9219]	9414; 9498 [9329]	10,099; 10,159 [9912]	9138; 9144 [9144]
N1	4124; 4114 [4085]	3237; 3249 [3263]	4107; 4108 [4070]	4057; 4057 [4054]	4047; 4031 [3966]	3472; 3455 [3276]
N3	3695; 3691 [3680]	3368; 3362 [3356]	3408; 3421 [3412]	3319; 3326 [3340]	3393; 3399 [3398]	3521; 3505 [3522]
C2	1657; 1653 [1652]	1667; 1662 [1665]	2317; 2313 [2307]	1546; 1545 [1548]	1758; 1753 [1745]	2027; 2023 [1993]
C4	2214; 2214 [2222]	2286; 2274 [2259]	2035; 2014 [1995]	2067; 2072 [2064]	2292; 2295 [2341]	2266; 2270 [2268]
C5	2942; 2959 [3029]	2944; 2964 [3067]	3753; 3727 [3776]	3120; 3138 [3200]	2783; 2792 [2848]	3165; 3164 [3161]
C6	1832; 1834 [1891]	1787; 1798 [1868]	2760; 2764 [2756]	2316; 2319 [2325]	1734; 1733 [1798]	1839; 1834 [1878]
H1	255; 255 [255]	277; 277 [277]	276; 267 [261]	282; 282 [282]	255; 254 [254]	252; 247 [243]
H3	249; 249 [242]	247; 247 [246]	248; 248 [249]	277; 278 [277]	276; 276 [276]	272; 272 [272]
H6	199; 200 [200]	198; 198 [197]	191; 191 [192]	195; 196 [195]	202; 202 [201]	199; 199 [198]

^a The values in each row are the magnitudes of C_Q for FU structures in free, separated, and [hybrid] forms. See Fig. 1 for the models.

stoichiometry of $C_4H_3FN_2O_2$. Parallel to the results of earlier studies on uracil, the di-keto form has been considered as the original model for the FU and the tautomers have been created based on the formations of keto-enol and di-enol forms [19–22]. To create the SiG model, hydrogen atoms are used to saturate the terminating atoms to avoid dangling effects at the tubular ends [23]. The B3LYP exchange–correlation functional and the 6-31G* standard basis set have been used to run all computations as implemented in the Gaussian 98 package [24]. Three sets of optimization processes have been performed to generate the stabilize structures. The first set of optimizations has been performed for the free FU structures and the second set have has been performed for the free SiG nanosheet. At the third set, the hybrid models including the SiG and FU tautomers together (Fig. 1) have been optimized to see the relaxation of each FU model on the surface of SiG nanosheet. For simplicity, the models obtained by the first and second steps of optimizations are not shown but the hybrid form of third set is shown in Fig. 1. To do optimizations for the hybrid models, the atomic positions of SiG have been kept frozen, but those of FU tautomers have been fully allowed to relax on the SiG surface. The optimized properties including delta total energies (ΔE_T), binding energies (E_B), energy levels for the highest occupied and the lowest unoccupied molecular orbitals (E_{HOMO} and E_{LUMO}), and dipole moments (D_M) have been evaluated for the investigated structures (Table 1). Moreover, the atomic properties of quadrupole coupling constants (C_Q) have been generated for the atoms of all optimized structures (Table 2) [25]. The details of molecular and atomic properties will be clarified by the following discussions. These computations have been performed to achieve the major purpose of this work to investigate the effects of SiG on the structures and properties of FU tautomers. Additionally, the properties for each tautomeric form of FU have been investigated using the computed results. Prior to experiments or to have a better clarifications of experiments, computations could yield insightful trends especially for the complicated nano and bio systems [26].

3. Results and discussion

3.1. Molecular properties

The evaluated molecular properties of the optimized structures (Fig. 1) are summarized in Table 1. The main molecular methodology of this work is to optimize possible di-keto, keto-enol, and di-enol structures of 5-fluorouracil (FU) on a silicon graphene nanosheet (SiG) model (Fig. 1). We have created two molecular systems of free FU structures and FU-SiG hybrids to investigate the effects of SiG on the properties of FU structures. We optimized both free and hybrid molecular systems to reach the minimum energies; however, the FU structures have been separated from the hybrid forms to make an exact investigation. The FU structures are differently relaxed on the surface of employed nanosheet as shown in Fig. 1; therefore, different properties are seen for the investigated hybrid systems. The single point energies for the optimized FU structures separated from the FU-SiG hybrids have been calculated to evaluate energies and other molecular properties. Our results of total energies and total energy differences (ΔE_T) indicated that the di-keto form (FU-0) is the most stable one among other structures in the free and hybrid forms, in which the keto-enol and di-enol structures are called possible tautomers of FU. Earlier works on the possible structures of uracil through tautomerism indicated that the di-keto form is still the most stable structure; however, the orders of stabilities are mainly dependent on the surrounding environments [19–22]. FU-1 is the most stable one and FU-2 is the most unstable one among the tautomers of FU, in which the oxygen number two is hydrogenated in FU-1 and the oxygen number four is hydrogenated in FU-2. The mentioned trend is in a direct agreement with the results of Yekeler and Özbakır [22] in their corresponding FU3 and FU5 tautomers. The orders of stabilities for both free and separated tautomers could be defined as FU-1 > FU-5 > FU-3 > FU-4 > FU-2 in agreement with the obtained results of Yekeler and Özbakır [22]. Comparing the energies of FU structures in the free and hybrid forms indicates that the stability is slightly reduced in the hybrid models showing the effect of SiG on the minimum energy of FU structures. The binding energies (E_B)

for the free and separated FU structures indicated that the formation di-keto form (FU-0) is still preferred regarding the other tautomers. Interestingly, the most and less favorability of formations are seen for FU-1 and FU-2 structures respectively, in agreement with their total energies results. The binding energies are slightly better for free structures than the separated ones referring to the effects of SiG on the stability reduction of FU tautomers. Moreover, the smallest interacting energy is seen for the di-keto FU-0 on the SiG nanosheet and the largest one is still seen for the FU-2 on the SiG nanosheet. Examining the magnitudes of energy levels for the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) indicate that the energy gaps between these two levels of FU structures are for both free and separated structures. For the hybrid FU-SiG structures, the energy gaps are significantly reduced due to the semiconductivity property of SiG nanosheet. The magnitudes of dipole moments indicate that the polarities for separated FU structures are larger than the free ones. Moreover, different value are observed for the tautomers showing the changes of molecular electronic properties with respect to the original di-keto form. The hybrid FU-SiG structures also show different values of dipole moments in comparison with free and separated FU structures. With the exception of FU-1-SiG and FU-2-SiG, the values of dipole moments for other FU-SiG structures are significantly reduced regarding the values of free and separated FU structures. As a brief conclusion of this section, it could be noted that the molecular properties of FU structures including the free and separated ones detect the effects of SiG nanosheet, in which the effects are more significant for the tautomers as seen by the values of ΔE_T and E_B showing the most stability for the di-keto form.

3.2. Atomic properties

The atomic properties have been investigated by the evaluated values of quadrupole coupling constants (C_Q) for the atoms of the optimized FU structures (Fig. 1) of free, separated, and hybrid models as summarized in Table 2. The interaction energy between the nuclear electric quadrupole moment (Q) and the z-axis eigenvalue of electric field gradient (EFG) tensors are measured as C_Q properties, which are experimentally measurable by the solid-state nuclear magnetic resonance (NMR) spectroscopy [27]. The arisen EFG tensors form the electronic sites of atoms could detect any perturbations to these sites [28]. Quantum computations could also yield reliable magnitude of C_Q properties for the investigated systems [29]. In addition to the evaluated molecular properties as discussed above, the atomic properties could show insightful trends on the electronic structures of matters. The C_Q properties are evaluated for all atoms of the FU structures in the forms of free, separated and hybrid models. The fluorine atom is the characteristic atom of FU structures with a large Q value, which are shown by the large magnitudes of C_Q properties for this atom. Although the F atom does not participate in the tautomeric process, but the effects of tautomerism could be seen for this atom among free and separated forms. Due to different positions of relaxed FU structures on the SiG surface in the hybrid models, changes the magnitudes of C_Q for the F atoms between separated and hybrid models show the additional effects of SiG nanosheet on the properties of FU tautomers. It is noted that the C_Q properties could be seen in different ways for the investigated models. Comparing the values of C_Q properties for the atoms of free and separated models could show that the tautomers detect different environments. Comparing the values of C_Q properties for the free or separated models with the hybrid models could show the significant effects of SiG nanosheet on the properties of FU structures. Therefore, an interested reader may achieve insightful trends about the FU tautomerization processes at the surface of SiG nanosheet by careful examination of the obtained values in the desired ways.

There are two oxygen atoms in the FU structure, which are in di-keto form for the original FU. However, keto-enol and di-keto forms are arisen through tautomerism for O2 and O4 atoms of resulted tautomers. The O2 atom is in the enol form in the FU-1, -3, and -4, and it is in the original keto form in the FU-0, -2, and -5 structures. The O4 atoms is in the enol form in the FU-2, -3, and -5, and it is in the original keto form in the FU-0, -1, and -4 structures. A quick look at the results reveals that the properties for O2 and O4 are different due to their different chemical environment, in which the O2 atom is a urea type oxygen and the O4 atom is an amide type oxygen. Moreover, yielding new keto and enol forms in the tautomerism processes also arise new properties for these two oxygen atoms. For the hybrid models, the position of FU structure at the surface of SiG nanosheet yields additional effects of nanosheet on the atomic properties of FU structures by following the values C_Q for O2 and O4 atoms. Similar trends are employed for the N1 and N3 atoms, which are mainly contributed to the tautomerism in the possible FU structures. Since the N atoms are the heterocyclic ring member atoms, they are significantly contributed to the tautomerism processes of FU structures. Moreover, the position of the relaxed FU structure on the surface of SiG nanosheet also arises additional effects for the properties of N1 and N3 atoms. The C2, C4, C5, and C6 atoms do not receive or release the H atom in the tautomerism processes, but their properties are significantly influenced by this process. The effects of SiG nanosheet are also meaningful for the C_Q properties of C atoms in the original and tautomeric FU structures by comparing the values for free, separated and hybrid models. Due to weak electron density, the orders of changes for the C_Q properties of H atoms are smaller than the F, O, N, or C atoms. The results show that the properties of H atoms are different among the tautomers but the effects are similar for each tautomer in the three free, separated, and hybrid models. It could be noted that although the positions of the H atoms are changed in the tautomeric systems, but the indirect effects on the other atoms are many more significant than own H atoms. As a conclusion of this section, it could be mentioned that the atomic properties of FU structures are significantly changed through tautomerism, in which the changes for F atom are the most significant among other atoms. Moreover, the environment of being or not being at the surface of SiG nanosheet also changes the properties of atoms and especially for the F atoms. Since the F atom is the characteristic atom of FU, changing its properties in the tautomerism and also in the hybrid models could determine the characteristic behavior of FU structures. It is known that the so many side effects of FU for patients encourages the researchers to characterize the

properties of FU in different environments to may find a way to reduce the side effects. In this work, we tried to show the significance of employing the SiG nanosheet as a relaxation substrate for the FU tautomers and following the resulted properties to reach a slightly better understanding of molecular level application of nanomatters in the life sciences.

4. Conclusions

Our DFT calculations of properties for different FU tautomers and SiG counterparts indicated that the effects of nanosheet are detected by tautomers. Comparing the molecular properties for different conditions indicates that the total and binding energies are changed through tautomerism both free and SiG hybrids. The results of optimizations indicated that the di-keto form is still the most stable structure among other ones. Examining the values of C_Q for atomic properties by C_Q properties of investigated compounds shows that the properties for F atom are significantly changed through tautomerization and SiG hybridization processes. Although the F atom does not contribute to the tautomerism process, but the indirect effects are detected by this atom making it as characteristic of FU structures. Moreover, the molecular and atomic properties showed the effects of nanostructure hybridizations could be well detected for the investigated tautomers.

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