The C–H···O Hydrogen Bonding Effects on the ^{17}O Electric Field Gradient and Chemical Shielding Tensors in Crystalline 1-Methyluracil: A DFT Study

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Dedicated to Prof. Mohamed Yalpani on the occasion of his 67th birthday

A density functional study was carried out to investigate the C–H···O hydrogen bonding effects on the ^{17}O electric field gradient and chemical shielding tensors in crystalline 1-methyluracil. Since the structural coordinates were obtained from a neutron diffraction study, no geometry optimization was needed in performing the calculations. It is demonstrated that C–H···O hydrogen bonding has different influences on O2 and O4 EFG and CS tensors. In the tetramer model of 1-methyluracil, which is much closer to the real crystalline phase, the influence of C–H···O on the O4 EFG and CS tensors is significant, whereas this influence is negligible for O2.

Key words: DFT; C–H···O Hydrogen Bonding; Electric Field Gradient Tensor; Chemical Shielding Tensor; 1-Methyluracil.

1. Introduction

Hydrogen bonding (HB) interactions are important in all fields of chemistry and biochemistry, especially between nucelobases in living systems [1]. Nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) spectroscopies are among the most versatile techniques to study the properties of different HB types [2, 3]. Electric field gradient (EFG) and chemical shielding (CS) tensors are very sensitive to the electron distribution around quadrupole and magnetic nuclei, respectively. Hence, in the hydrogen bond systems, the tensors eigenvalues of those nuclei contributing to the HBs will change significantly. Among the various HB types, studying the properties of unusual HB types, e.g., C–H···O, is an interesting subject [4 – 6]. However, there is less attention to characterize these HB types rather than classical HB types in the literature.

Previous studies indicated that uracil and its derivatives are capable of making HBs [7 – 12]. 1-Methyluracil (1-MU) is the simplest uracil N(1)-derivative which can be used as a model molecule in the investigation of the structural properties of uracil due to the N(1)-derivation. However, to the best of our knowledge there are almost no systematic NQR and NMR data of 1-MU in the literature. The calculated results were compared with available experimental data of crystalline uracil [10]. One of the advantages of computational studies is the possibility to consider the various effects individually. Therefore, the present computational study focuses on the influence of C–H···O HBs on the ^{17}O EFG and CS tensors in crystalline 1-MU via the density functional theory (DFT). Hence, a complete characterization of the C–H···O HB properties is achieved in this study. Quadrupole coupling constants (C_Q), asymmetry parameters (η_Q) and isotropic chemical shifts (δ_{iso}) obtained from the calculated ^{17}O EFG and CS tensors are exhibited in Table 1.

2. Computational Aspects

All the calculations were carried out based on the density functional theory (DFT) via Gaussian 98 package [13]. The employed method is the B,LYP exchange functional [14, 15]. The basis sets are 6-311++G**, 6-311+G*, 6-31++G**, and 6-31+G*. To calculate the ^{17}O CS tensor, the gauge including atomic orbital (GIAO) [16] approach was used. The quantum calculations yield principal components of EFG and CS tensors in the principal axes system (PAS). To have a direct relation with the experiment, these components

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Table 1. The calculated ^{17}O NQR and NMR parameters.

Nucleus /	Basis set	C_Q (MHz)	η_Q	δ_{iso} (ppm)
O2	6-311++G**	8.98; 8.79; 8.99	0.33; 0.38; 0.34	317; 310; 315
	6-311+G*	9.97; 8.78; 8.98	0.34; 0.38; 0.35	315; 309; 314
	6-31++G**	8.43; 8.22; 8.40	0.41; 0.46; 0.43	279; 273; 275
	6-31+G*	8.44; 8.23; 8.41	0.41; 0.46; 0.43	280; 273; 275
	Expt.[a]	7.61	0.50	245
	Comp.[b]	8.48	0.44	278
O4	6-311++G**	10.1; 9.79; 8.73	0.14; 0.21; 0.42	411; 389; 336
	6-311+G*	10.1; 9.77; 8.71	0.14; 0.22; 0.43	409; 386; 333
	6-31++G**	9.43; 9.07; 8.03	0.21; 0.29; 0.51	365; 343; 294
	6-31+G*	9.43; 9.08; 8.04	0.21; 0.29; 0.51	364; 342; 293
	Expt.[a]	7.85	0.55	275
	Comp.[b]	8.15	0.61	300

In each column the first number belongs to the monomer, the second one belongs to the target molecule in trimer and the third one belongs to the target molecule in tetramer 1-MU.

[a] The experimental values for uracil are from [10].

[b] The computational values for uracil at the level of B3LYP/6-311++G** are from [7] where the absolute shielding (^{17}O) of 307.9 is used as reference of δ_{iso}.

Table 2. Relative orientations of the ^{17}O EFG and CS tensors.

Nucleus /	Basis set	α (°)	β (°)	γ (°)
O2	6-311++G**	1; 1	90; 90	80; 99
	6-311+G*	1; 1	90; 90	80; 99
	6-31++G**	1; 1	90; 90	81; 81
	6-31+G*	1; 1	90; 90	81; 81
	Expt.[a]	0	89	82
O4	6-311++G**	180; 180	90; 90	82; 100
	6-311+G*	0; 180	90; 90	82; 99
	6-31++G**	0; 180	90; 90	98; 79
	6-31+G*	0; 180	90; 90	98; 79
	Expt.[a]	0	90	75

In each column the first number belongs to the target molecule in trimer and the second one belongs to the target molecule in tetramer 1-MU.

[a] The experimental values for uracil are from [10].

were converted to the parameters observed experimentally.

The EFG tensor components were converted to the quadrupole coupling constant, C_Q, and the asymmetry parameter, η_Q, see (1) and (2). In (1), the standard value of the quadrupole moment, Q, of ^{17}O was used as 25.58 mb [17]. The asymmetry parameter indicates the deviation of the electron distribution around the nucleus from axial symmetry and is an important parameter in quadrupole interactions:

$$C_Q\ (\text{MHz}) = e^2 Q q_{zz} h^{-1}, \tag{1}$$

$$\eta_Q = |(q_{xx} - q_{yy})/q_{zz}|. \tag{2}$$

The CS tensor components were also converted to the isotropic chemical shift, δ_{iso}, see (3), where the absolute chemical shielding constant of ^{17}O in liquid H_2O, 307.9 ppm [18], was used as reference:

$$\delta_{\text{iso}}\ (\text{ppm}) = 307.9 - \sigma_{\text{iso}}. \tag{3}$$

The calculated ^{17}O C_Q, η_Q and δ_{iso} of the monomer and the target molecule in the trimer and tetramer 1-MU are exhibited in Table 1. The relative orientations of the ^{17}O EFG and CS tensors of the target molecule in the trimer and tetramer 1-MU are presented in Table 2.

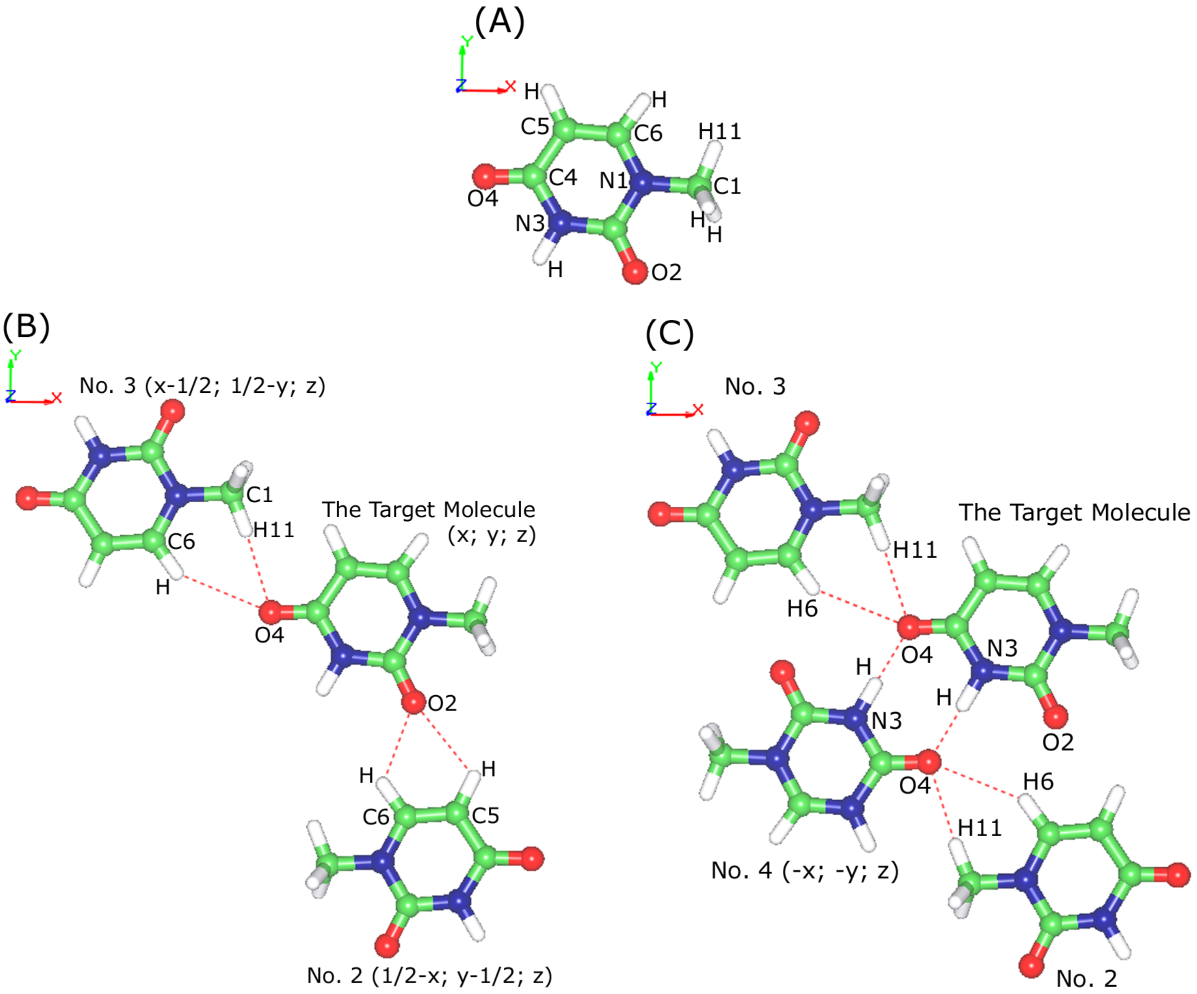
Table 3. The intermolecular C–H···O and N–H···O HB distances and angles.

C–H···O	Distance (Å)	Angle (°)
C5–H(No. 2)···O2	2.60	115.5
C6–H(No. 2)···O2	2.36	123.8
C6–H(No. 3)···O4	2.77	148.4
C1–H11(No. 3)···O4	2.32	176.4
N3–H(No. 4)···O4	1.77	179.5
N3(No. 4)···O4	2.81	

3. Results and Discussion

To include the C–H···O HB type in the calculations, two crystalline models of 1-MU were created using coordinate transforming (see Scheme 1). Considering the presence of C–H···O HBs, a trimer model was created, whereas considering the chemical moieties of oxygen nuclei much closer to the real crystalline phase, a tetramer model of 1-MU was also created. Since the coordinates of 1-MU were obtained from neutron diffraction at 60 K [19], geometry optimization was not needed in this study. To have an observation of HB effects on the ^{17}O EFG and CS tensors, the calculations were performed for monomer, trimer and tetramer models of 1-MU. Having a direct relation with the experiments, the calculated ^{17}O EFG tensors were converted to C_Q and η_Q and the calculated ^{17}O CS tensors were converted to δ_{iso}, see (1)–(3). The calculated parameters, C_Q, η_Q and δ_{iso}, are listed in Table 1. As mentioned in Section 2, the calculations were carried out employing four basis sets. Since earlier studies indicated more reliability of 6-311++G** results [6, 7, 10, 20–23], in the following text, the results of this basis set will be referred to. The relative orientations of the ^{17}O EFG and CS tensors in the molecular frame of reference (α, β, γ) for the target molecule in trimer and tetramer 1-MU were also calculated and are reported in Table 2.

There are two types of oxygen nuclei in 1-MU where O2 is a urea type and O4 is an amide type



Scheme 1. (A) The monomer, (B) the trimer, (C) the tetramer 1-MU. The dashed lines show intermolecular C–H···O and N–H···O HBs.

of oxygen. Previously, both mentioned forms of oxygen were studied extensively by Wu and co-workers [24, 25]. In the following, the influence of C–H···O HB types on ^{17}O EFG and CS tensors will be discussed separately.

3.1. *The ^{17}O Electric Field Gradient Tensor*

The calculated ^{17}O EFG results of the monomer, the target molecule of the trimer and that of the tetramer crystalline 1-MU are presented in Table 1. It is well known that the C–H···O HB type deviates from the classical definition of HBs. So its strength is smaller than that of the N–H···O or O–H···O HB types. By a quick look at the calculated results of monomer and trimer 1-MU, the influence of this HB type on the ^{17}O EFG tensor of both urea type, O2, and amid type, O4, can be observed. Because of C-H···O, the $C_Q(^{17}\mathrm{O2})$ and $C_Q(^{17}\mathrm{O4})$ reduce by 0.19 and 0.31 MHz, respectively. O2 interacts with C5-H and C6-H of molecule 2 with the intermolecular distances of 2.60 and 2.36 Å, respectively (see Table 3). The angle of C5–H···O2 is 115.5° and that of C6–H···O2 is 123.8°. Since the HBs are mainly dependant on the intermolecular distance and the angle of interaction, it seems that the influence of C6–H is greater than that of C5–H on the ^{17}O EFG tensor of O2 because of the shorter intermolecular distance and greater planarity.

For O4, there are also two possible of interactions, C1–H11···O4 and C6–H···O4, with molecule 3. The intermolecular distances are 2.32 and 2.77 Å, respectively. Their angles are 176.4° and 148.4°, respectively. In agreement with O2, C–H···O HBs influence on the ^{17}O EFG tensor of O4. $C_Q(^{17}\text{O4})$ reduces by 0.12 MHz more than that of O2. Besides, the deviation of η_Q for O4 is a magnitude of 0.03 more than that of O2. More significant C_Q and η_Q changes of O4 rather than those of O2 reveal more influence of C–H···O HBs on the O4 EFG tensor rather than that of O2 in trimer 1-MU.

When the model of 1-MU was grown to tetramer, different values of C_Q were observed for O2 and O4 compared to those of the trimer. The target molecule of the tetramer 1-MU contributes to N–H···O HBs with molecule 4 (see Scheme 1). N–H···O has a direct influence on O4, where $C_Q(^{17}\text{O4})$ reduces to 8.73 MHz from monomer to tetramer. This significant reduction indicates the importance of N–H···O HBs on the O4 EFG tensors. On the other hand, the presence of molecule 4 influences the O2 EFG tensors of the target molecule, indirectly. The O4 of molecule 4 interacts with the H6 and H11 of molecule 2 through C–H···O HBs. The situation of this interaction is the same as the C–H···O interaction of the target molecule with molecule 3. Comparison of the $C_Q(^{17}\text{O2})$ of the target molecule in the tetramer with that of the monomer 1-MU indicates the negligible role of O2 in the C–H···O HB in the tetramer 1-MU. These results indicate that O4 plays the major role in the C–H···O HB, while that of O2 is negligible.

3.2. The ^{17}O Chemical Shielding Tensor

In the previous subsection the sensitivity of the ^{17}O EFG tensor to the presence of HBs was shown. In this subsection, the influence of C–H···O on the ^{17}O CS tensor will be discussed by comparing the values of δ_{iso} in the monomer and the target molecules in trimer and tetramer 1-MU. By a quick look at the calculated δ_{iso} in Table 1, one can easily observe that, similar to the ^{17}O EFG tensor, HBs also influence the ^{17}O CS tensors of O2 and O4 nuclei. It was found that the influence of HBs on the $C_Q(^{17}\text{O4})$ is greater than that of O2. Similarly, it was observed that the $\delta_{\text{iso}}(\text{O4})$ reduces by 15 ppm more than that of O2 from monomer to trimer 1-MU. Besides, similar to the $C_Q(^{17}\text{O4})$, which was placed in the upper-field rather than that of O2, the $\delta_{\text{iso}}(\text{O4})$ is placed in an upper-field rather than that of O2.

Because of the N–H···O presence in the tetramer 1-MU, HBs have a more significant influence on the O4 CS tensor. From the EFG results, it was indicated that O4 contributes to C–H···O while the role of O2 in this interaction is negligible. Comparison of the values of $\delta_{\text{iso}}(\text{O2})$ in the two forms of the monomer and the target molecule in the tetramer 1-MU reveals the negligible influence of HBs on the O2 CS tensor. The calculated ^{17}O EFG and CS tensors demonstrate a harmony in the determination of the HB influence. Therefore, for the interpretation of H-bond systems, the calculation of the ^{17}O EFG and CS tensors is an advantage.

3.3. Orientations of the ^{17}O EFG and CS Tensors

One of the benefits of quantum calculations is determining the orientations of EFG and CS tensors in the molecular frame of reference. Experimentally, relative orientations of the EFG and CS tensors can be determined by solid-state NMR. Wu and co-workers have extensively studied the ^{17}O EFG and CS tensors of several compounds both experimentally and computationally [7, 10, 24, 25].

In this work, the relative orientations of the ^{17}O EFG and CS tensors in the molecular frame of reference were determined for O2 and O4 of the target molecules in trimer and tetramer 1-MU (see Table 2). The results reveal that in trimer 1-MU, the smallest component of the EFG, q_{xx}, and the largest component of CS, σ_{33}, are parallel and in the same direction in O2. However, for O4 the direction is reversed. On the other hand, the angle between q_{zz} and σ_{33}, β, is 90° for both O2 and O4. The angle between the largest component of EFG, q_{zz}, and the smallest component of CS, σ_{11}, γ, is 80° for O2 and 82° for O4. Both α and β reveal that in the trimer 1-MU q_{xx} and σ_{33} are perpendicular to the molecular plane, while γ indicates that q_{zz} and σ_{11} are in the molecular plane. From trimer to tetramer the values of α and β don't change for O2, while the angle between q_{zz} and σ_{11} differs, $\gamma = 99°$. Similarly, α and β don't change for O4 but γ differs, $\gamma = 100°$.

3.4. Comparing with the Experiment

As mentioned earlier, to the best of our knowledge there exist no experimental solid-state NMR data for 1-MU in the literature. Therefore, the available experimental and computational solid-state NMR data of uracil [7, 10] were used. In the crystalline phase of uracil, O2 contributes to two C–H···O HBs while O4 contributes to C–H···O and N–H···O HBs. Comparing with tetramer 1-MU, O2 almost contributes to no HBs, hence there is a completely different situation for O2 in uracil and 1-MU. On the other hand, the situation of O4 is the same in uracil and tetramer 1-MU. However, because of the different intermolecular geometrical parameters which are caused by N(1)-derivation, the exact experimental and computational values of the O4 EFG and CS tensors are reasonably different in uracil and 1-MU. But, comparison of the computational NMR data of uracil at the level of B3LYP/6-311++G** with those of 1-MU exhibits a harmony in the upper-field and lower-field beings of the mentioned values. A comparison of the uracil and 1-MU results also reveals that the function of uracil is changed due to N(1)-derivation.

4. Conclusion

The preceding work was a computational NQR and NMR study to investigate the influence of C–H···O HBs on the ^{17}O EFG and CS tensors of the target molecule in trimer and tetramer crystalline 1-MU. Although the results of trimer 1-MU demonstrate the influence of C–H···O HBs, but because of the greater similarity of the tetramer 1-MU to the real crystalline phase, the results of the tetramer 1-MU are more comparable with the experiment. From the calculated parameters, some trends are concluded. First, it was observed that C–H···O influences the ^{17}O EFG and CS tensors. This trend indicates that in proper geometrical properties, oxygen will contribute to C–H···O HBs which also agrees with the recent study of Grunenberg [4]. Second, the influence of C–H···O on O4 is significant while that of O2 is negligible. Third, comparing the results of this work with the available experimental data of uracil [10] reveals that the function of uracil is changed due to N(1)-derivation. Fourth, the agreement between the calculated ^{17}O EFG and CS tensors indicates the benefit of both tensor calculations in the characterization of H-bond systems. Fifth, since the values of calculated tensors are different in the forms of monomer and cluster, the employed method, B3LYP, and basis sets, 6-311++G**, 6-311+G*, 6-31++G** and 6-31+G*, can reproduce reliable results in the characterization of C–H···O HB effects on the ^{17}O EFG and CS tensors. There is also an agreement between the calculated results of this study and those of previous similar studies [7, 10].

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