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Density functional calculations of oxygen, nitrogen and hydrogen electric field gradient and chemical shielding tensors to study hydrogen bonding properties of peptide group (O=C–NH) in crystalline acetamide

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Abstract

A density functional theory (DFT) study was carried out to investigate hydrogen bonding (HB) properties of peptide group (O=C–NH) in crystalline acetamide. Since the peptide group in acetamide contributes to N–H···O and C–H···O types of HB interactions, acetamide is considered as the simplest form of peptide linkage in proteins. The evaluated NMR parameters including quadrupole coupling constants and asymmetry parameters from the calculated electric field gradient (EFG) tensors at the sites of O17, N14 and H2 nuclei and isotropic chemical shieldings from the calculated chemical shielding (CS) tensors at the sites of O17, N15 and H1 nuclei reveal the major contribution of O=C–NH group to HB interactions. Although N–H···O type of HB interaction play the major role in the HB properties of peptide group in lattice form of crystalline acetamide, however, the role of weaker C–H···O type of HB interaction cannot be neglected.

Keywords: DFT; NMR; Hydrogen bond; Peptide; Acetamide

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1. Introduction

Hydrogen bonding (HB) interactions play unique roles in various living systems, e.g., in determination of the structural properties and also in stabilization of the β-sheets in proteins [1]. Because the macromolecular protein structures are very complex to study, studying the simplest models having the major characteristic of proteins is an advantage in the investigation of HB properties in these structures. Acetamide with a single peptide group (O=C–NH) can be considered as the simplest model system of peptide linkage in proteins and polypeptides. Acetamide is capable of contributing to N–H···O=C and C–H···O=C types of HB interactions which are very important in the stabilization of α-helix and β-sheet structures and numerous studies using various techniques were devoted to characterize the properties of them [2–14].

Since the most characteristic nature of HB is electrostatic, those techniques dealt with this nature are proper in the investigation of HB properties. Among them, nuclear magnetic resonance (NMR) spectroscopy is an important technique to study the properties of various types of HB interactions. Electric field gradient (EFG) and chemical shielding (CS) tensors arisen by the electronic environment at the sites of quadrupole nuclei, e.g., ^{17}O, ^{14}N and ^{2}H, and magnetic nuclei, e.g., ^{17}O, ^{15}N and ^{1}H, respectively, are significantly influenced by HB interactions and are such useful elements to study HB interactions properties in the considered hydrogen bonded systems [15,16].

Present work calculates NMR tensors (EFG and CS) at the sites of oxygen, nitrogen, and hydrogen nuclei to study the properties of HB interactions of the peptide group (O=C–NH) in acetamide. To this aim, the crystalline coordinates of acetamide at 146 K was obtained from X-ray study of Bats et al. [17] and the hydrogen bonded six-molecule lattice consisting of those the most possible HB interacting molecules through N–H···O and C–H···O HB types was created by coordinates transforming (see Table 1 and Fig. 1). To systematically

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Table 1
The geometrical properties of acetamide

Intramolecular	Before H-optimization[a]	After H-optimization[b]
rN–H1	0.90 Å	1.01 Å
rN–H2	0.87 Å	1.02 Å
rC1–O	1.24 Å	1.24 Å
rC2–H	0.98 Å	1.09 Å
Intermolecular		
rN···O [No. 3]	2.93 Å	2.93 Å
rN···O [No. 2]	2.87 Å	2.87 Å
rN–H1···O [No. 3]	2.03 Å	1.94 Å
rN–H2···O [No. 2]	2.01 Å	1.86 Å
rO···N [No. 3]	2.99 Å	2.99 Å
rO···C2 [No. 4]	3.47 Å	3.47 Å
rO···N [No. 5]	2.87 Å	2.87 Å
rO···H1–N [No. 3]	2.05 Å	1.90 Å
rO···H–C2 [No. 4]	2.49 Å	2.37 Å
rO···H2–N [No. 5]	2.01 Å	1.86 Å
rC2···O [No. 6]	3.47 Å	3.47 Å
rC2–H···O [No. 6]	2.49 Å	2.37 Å
∠N–H1···O [No. 3]	117.6°	162.6°
∠N–H2···O [No. 2]	168.1°	168.3°
∠O···H1–N [No. 3]	171.6°	169.4°
∠O···H–C2 [No. 4]	177.8°	176.4°
∠O···H2–N [No. 5]	168.1°	163.8°
∠C2–H···O [No. 6]	177.7°	177.8°

See Fig. 1 for details.

[a] The original coordinates from reference [17] are considered.

[b] The H positions of original coordinates are just optimized.

investigate the HB properties of O=C–NH group in the considered system, the NMR tensors were calculated for acetamide in its monomer, a representative dimer and lattice crystalline forms. Table 2 presents the quadrupole coupling constants (C_Q) and asymmetry parameters (η_Q) evaluated by the calculated EFG tensors at the sites of ^{17}O, ^{14}N and ^{2}H nuclei and Table 3 presents the isotropic chemical shieldings (σ_{iso})

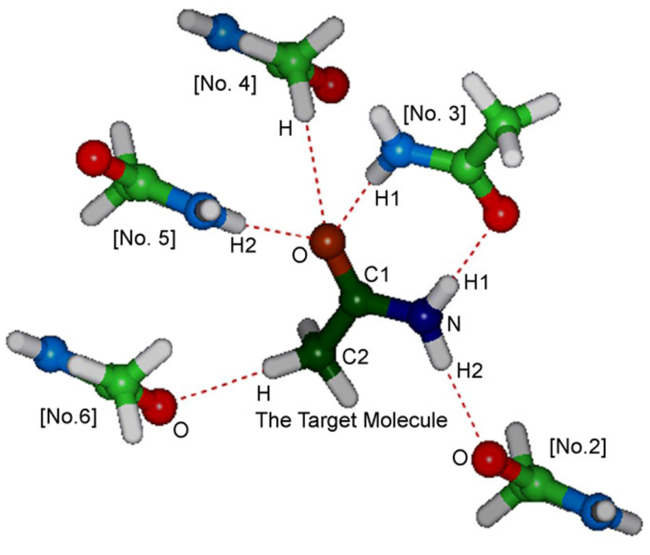

Fig. 1. The six-molecule lattice of crystalline acetamide. In monomer model, just the target molecule and in dimer model, the target molecule and molecule [No. 3] are considered. Dash lines show HB interactions (see Table 1 for details).

Table 2
The EFG tensors at the sites of ^{17}O, ^{14}N and ^{2}H nuclei

Nucleus	C_Q (MHz)[a]						η_Q[a]					
	Monomer[b]		Dimer[c]		Lattice[d]		Monomer[b]		Dimer[c]		Lattice[d]	
	Before[e]	After[f]	Before[e]	After[f]	Before[e]	After[f]	Before[e]	After[f]	Before[e]	After[f]	Before[e]	After[f]
^{17}O	10.1 [10.1]	9.90 [9.86]	9.54 [9.48]	9.17 [9.09]	8.81 [8.76]	8.48 [8.45]	0.12 [0.13]	0.16 [0.17]	0.25 [0.26]	0.32 [0.33]	0.42 [0.44]	0.51 [0.52]
^{14}N	3.58 [3.70]	4.27 [4.43]	3.06 [3.18]	3.55 [3.70]	2.53 [2.64]	2.86 [3.01]	0.22 [0.17]	0.08 [0.09]	0.39 [0.33]	0.38 [0.36]	0.65 [0.56]	0.32 [0.25]
$^{2}H1$	547 [532]	266 [255]	551 [538]	230 [220]	522 [507]	236 [226]	0.12 [0.11]	0.17 [0.16]	0.13 [0.13]	0.20 [0.20]	0.11 [0.11]	0.19 [0.18]
$^{2}H2$	653 [636]	262 [250]	671 [655]	263 [251]	630 [613]	220 [211]	0.12 [0.11]	0.19 [0.18]	0.11 [0.10]	0.17 [0.16]	0.11 [0.10]	0.19 [0.18]
^{2}H	377 [369]	202 [194]	378 [370]	205 [196]	368 [360]	181 [176]	0.02 [0.02]	0.02 [0.02]	0.02 [0.02]	0.03 [0.02]	0.02 [0.03]	0.04 [0.04]

[a] The values in brackets are for 6-311+G* basis set and those out of brackets are for 6-311++G** one. The C_Q values of ^{2}H are in kHz.

[b] Crystalline monomer.

[c] Crystalline dimer including the target and molecule No. 3 (see Fig. 1), the values are averaged for two molecules.

[d] The target molecule in lattice (see Fig. 1).

[e] Before H-optimization.

[f] After H-optimization.