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The Role of the Linearity on the Hydrogen Bond in the Formamide Dimer: a BLYP, B3LYP, and MP2 Study

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Abstract. Quantum chemistry methods have been proven to be a very useful tool to study chemical systems stabilized by hydrogen bonds. The two theoretical methodologies most frequently used are the Density Functional Theory (DFT), in its Kohn-Sham version, and the second order Møller-Plesset Perturbation Theory (MP2). Lately, many studies have been focused on weak hydrogen bonds (binding energies < 4 kcal/mol) because such contacts might have a relevant role in the molecular ensemble. However, there are some results about this type of interactions where the Kohn-Sham model and MP2 give different answers. By testing two exchange-correlation functionals, BLYP and B3LYP, we are proposing in this paper that such a discrepancy will happen mainly when the hydrogen bond is far from the linearity; we present this hypothesis on the formamide dimer as an example. We found that, even when this dimer exhibits two hydrogen bonds (N-H...O) with moderate strength, the MP2 and the two exchange-correlation functionals, considered in this work, predict different potential energy surfaces when the geometrical parameters of the hydrogen bond are distorted and a limited basis set is used.
Key words: Hydrogen bond, DFT, MP2, Theoretical approach, Basis set functions, Formamide dimer.

Resumen. Los métodos de la Química Cuántica han probado ser una herramienta muy útil para el estudio de sistemas estabilizados por puentes de hidrógeno. Las dos metodologías teóricas más frecuentemente empleadas son la Teoría de Funcionales de la Densidad (TFD), en la versión de Kohn-Sham, y la Teoría de Perturbaciones a Segundo Orden de Møller-Plesset (MP2). Recientemente muchos estudios se han enfocado a los puentes de hidrógeno débiles (con energías de enlace < 4 kcal/mol), ya que se ha encontrado que tales contactos pueden jugar un papel importante en la asociación molecular. Sin embargo, existen algunos resultados sobre este tipo de interacciones donde el modelo de Kohn-Sham y MP2 dan resultados diferentes. Haciendo la prueba con dos funcionales de intercambio y correlación, BLYP y B3LYP, en este estudio proponemos que estas diferencias pueden ocurrir, principalmente, cuando el puente de hidrógeno se aleja de la linealidad. En este sentido, este trabajo presenta un estudio sobre el dímero de formamida como un ejemplo para probar esta hipótesis. Nosotros encontramos que, aun cuando en este dímero se presentan puentes de hidrógeno de fuerza moderada (N-H...O), MP2 y los dos funcionales de intercambio y correlación considerados, difieren en la predicción de la superficie de energía potencial cuando los parámetros geométricos del puente de hidrógeno están distorsionados y si se usa un conjunto de base limitado.
Palabras clave: Puentes de hidrógeno, TFD, MP2, estudio teórico, conjunto de funciones de base, dímero de formamida.

Introduction

Hydrogen bond is a peculiar interaction in nature, which gives special characteristics to those materials that contain it [1]. Let us take as an example one of the most common hydrogen bonds, the interaction found between water molecules. The hydrogen bond present in water provides it the property, for example, to be a liquid in a wide range of temperatures with a high boiling point [2]. For water, these effects are provoked even when the previously mentioned interaction represents only the five percent of a covalent bond involved in a water molecule [3]. Thus, this “weak interaction” makes water a unique and vital substance.

Although the strength of a hydrogen bond is not as big as a covalent bond, it is able to control a molecular ensemble due to its directionality and cooperative effects, in this way it is known that the Kevlar® polymer has a tidy structure where the involved hydrogen bonds generate well packed fibers [4]. In other cases, an intricate hydrogen bonds web is the main responsible of the 3D structures in proteins [5].

The type of interactions mentioned above involves *conventional* hydrogen bonds where the O-H...O in the water or the N-H...O found in the Kevlar® and proteins, are contacts where the acceptor and donor atoms are electronegative. Recently, it has been recognized another sort of hydrogen bonds where the donor is an atom with low or moderate electronegativity, and with a weaker strength than that observed in *conventional* hydrogen bonds [6]. Many of the evidences of these *weak* hydrogen bonds, comes from diffraction methods, and they can be found in biomolecules, organic molecules, organometallic compounds and inclusion complexes.

Particular cases of such an interaction are the C-H...O and the C-H...N hydrogen bonds, where the acceptor atom can be oxygen or nitrogen, and the donor is the carbon atom. The role of this interaction on the structural stabilization in molecular systems is still in debate, although the number of studies recognizing the importance of this interaction is increasing. As examples, we can mention its relevance on the molecular conformation and crystal packing, on molecular recognition processes and on the stabilization of inclusion complexes [6].

On the other hand, theoretical methods have been used to estimate the binding energies of these non-conventional hydrogen bonds and they have proved, in some systems, that this is a very important stabilizing force [7]. Previously, we estimated in four conformers of the *N*,*N*-dimethylformamide dimer the strength of the C-H interaction, with the C=O group, in approximately 2.1 kcal/mol [8]. In the same report, by using a linear correlation between C-H...O bond energies and gas-phase proton affinities, we reported the ΔH^{298} for the C^{α}-H...O=C hydrogen bond in around 3.0 kcal/mol, about 2.3 kcal/mol less than the N-H...O=C hydrogen bond strength. This fact implies that the C^{α}-H...O=C hydrogen bonds involved in proteins are strength enough to play an important role in the stabilization of secondary and ternary structure of these systems.

The estimations published in the reference [8] were obtained with the Møller-Plesset second order perturbation theory (MP2) [9], and they were compared with different exchange-correlation functionals within the Density Functional Theory (DFT) context [10]. The local density approximation (LDA) [11] using a triple-ς basis set [12] gave us the order predicted by MP2 with a much bigger basis set (aug-cc-pVTZ) [13], but the binding energies were overestimated, which is a well-known behavior of this exchange-correlation functional. The hybrid exchange-correlation functional (B3LYP) [14] reproduced the same energy order than MP2 for two of the analyzed conformers, those whose hydrogen bond angles were more linear. However, for the two conformers with a stacking conformation, the DFT binding energies were in disagreement with the MP2 results. This type of results is an example where some authors claim a DFT failure to predict hydrogen bonds. Currently, the MP2 method is accepted as a reference in the literature to describe weak hydrogen bonds. It is important to point out some nuances about the topic if DFT describe correctly hydrogen bond contacts.

There are many examples where the DFT performance has shown its reliability to estimate distances, angles and binding energies of strong and moderate hydrogen bonds (4-40 kcal/mol). It is known that the generalized gradient approximation (GGA) and hybrid exchange-correlation functionals give good estimations for binding energies and geometries in this sort of hydrogen bonds, but the LDA always overestimates binding energies and predicts short hydrogen bond distances [15].

For weak hydrogen bonds (< 4 kcal/mol), DFT some times fails even with hybrid exchange-correlation functionals. However, in some systems DFT works well, for example, by using the MP2 and DFT methods we found an adduct formed by the 1,4-benzoquinone (BQ) and the benzoic acid, stabilized by O-H...O and C-H...O hydrogen bonds [16]. Such a work showed that the hydrogen atoms of the BQ are acidic enough to form hydrogen bonds, which is in agreement with the experimental finding for the BQ in its crystal structure where C-H... O contacts are observed. The estimation we made for the C-H... O energy hydrogen bond in the adduct between BQ and benzoic acid, using B3LYP/TZVP [17a] was in agreement with the MP2 results previously reported [17b, 17c]. Like this one, we may cite other reports where DFT works well even when the hydrogen bond is weak. Then, which are the cases where DFT will fail? We are giving in this work some findings in this direction.

Our proposal in this paper is to show that when the hydrogen bond does not have a favorable geometry, it means that the hydrogen bond angle is far from the linearity, DFT will not properly describe the contact or at least the results will differ from MP2 predictions, even on *conventional* hydrogen bonds. To prove this, we present the study of the formamide dimer where the most stable conformer present two hydrogen bonds of moderate strenght.

The formamide dimer is a well-known system; its conformers have been characterized with different methodologies [18]. The most stable conformer is stabilized by two conventional N-H...O=C hydrogen bonds, which binding energy is about 7.1 kcal/mol. This type of contacts is the reason we picked this system to prove our hypothesis, because this hydrogen bond is not weak and we would expect that DFT or MP2 give similar results each other. We will show in this paper that when the geometrical parameters of the hydrogen bonds are distorted this will not happen, if we do not take care of the basis set used.

Methodology

The formamide molecule and its most stable dimer [18] were optimized at the Hartree-Fock (HF) [9b] level of theory with the 6-311G** basis set [19]. In this dimer, two N-H...O contacts were observed as it is shown in the Figure 1a. It is important to point out that we do not want to characterize this dimer because it was already done [18], the HF geometry is used to have a fixed geometry and on this geometry we will compare the results obtained with DFT and MP2. Of course, we decided to use this geometry as reference, but we could be used a DFT or MP2 geometry, or if it could be possible, the experimental geometry. Thus, taking this geometry we performed a scan from 0º (Figure 1a) to 180º (Figure 1b) of the dihedral angle defined by the O---N-C-O atoms as it is described in the same Figure 1. This dihedral angle was changed by 10º each time,

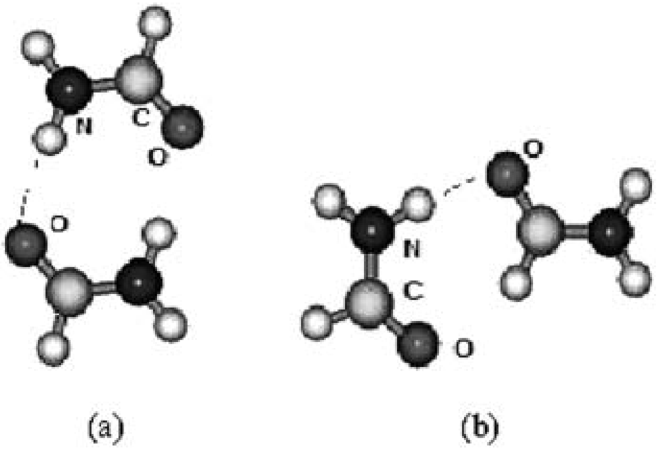

Fig. 1. Structures involved in the potential energy surface scan of the most stable formamide dimer, from 0º (a) to 180º (b).

Table 1. Geometrical parameters for the most stable formamide dimer. In this case we are reporting the geometrical parameters corresponding to the two hydrogen bonds. The distances are in angstroms and angles in degrees.

Method	D(O...H)	D(O...N)	< O...H-N
HF/6-311G**	2.02	3.01	169.5
MP2/DZP[a]	1.99	2.99	169.7
MP2/aug-cc-pVTZ[b]	1.83	2.84	174.2
MP2/6-311G**	1.90	2.91	173.3
	1.89	2.91	173.3
MP2/cc-pVTZ	1.79	2.81	175.3
BLYP/6-311G**	1.88	2.91	173.2
	1.88	2.91	173.1
BLYP/cc-pVTZ	1.87	2.90	173.4
B3LYP/6-311G**	1.88	2.90	172.5
	1.87	2.90	172.5
B3LYP/cc-pVTZ	1.87	2.89	172.9

[a]Ref. 22, [b]Ref. 18

and the dimer geometry was optimized in each step fixing the O---N-C-O dihedral angle.

For each step in the scan, a single point calculation of the dimer was computed by using the MP2 [9] method, the BLYP [20] and the B3LYP [14] exchange-correlation functionals within the DFT context, all of them with the 6-311G** basis set. As we mentioned above, a fixed geometry is necessary to carry out the comparison between both methods. Additionally, for three dihedral angles (0º, 90º and 180º) the dimer geometries at HF/6-311G** were re-optimized at the MP2/6-311G**, BLYP/6-311G**, and B3LYP/6-311G** levels.

Furthermore, for the dihedral angles 0º, 80º, 90º, 100º, and 180º the dimer geometries obtained with HF/6-311G** were re-optimized with the HF/cc-pVTZ level of theory, and for three dihedral angles (0º, 90º and 180º) the dimer geometries were optimized with the MP2/cc-pVTZ, BLYP/cc-pVTZ and B3LYP/cc-pVTZ methods. All calculations were done with the NWChem v4.5 program [21].

Results and Discussion

The geometrical parameters for the hydrogen bonds presented in the most stable dimer (Fig. 1a), are reported in Table 1. It is observed, in this table, that the HF method gives very similar results than MP2/DZP results reported previously [22]. When the basis set is increased [18], the distances are shorter and the hydrogen bond angle is more linear in about 2.8 % than the previous basis set. However, the MP2 and DFT methods describe almost the same geometrical parameters when the aug-cc-pVTZ basis set is used (reported previously in ref.18) and also with the 6-311G** basis set of this work, because they differ in 0.5 % in the N-H...O hydrogen bond angle. Comparing the DFT (BLYP and B3LYP) calculations using the 6-311G** and the cc-pVTZ basis set, the distances and angles are very similar each other (they do not differ in more than 0.5 %). But when MP2 is used, the distances are shorter (~5 %) and the hydrogen bond angle is more linear (~1 %) with the cc-pVTZ basis set. The effect of the basis set on the geometry and energetic on this dimer is widely discussed in Ref. 18.

The scan of the potential energy surface (PES) obtained with the HF/6-311G** and MP2/6-311G**//HF/6-311G** methods is depicted in Figure 2. From this plot we can see that the difference observed between both methods start from 70º and remains almost constant until 180º. Clearly the MP2 method increases the energy from the HF values for almost 1 kcal/mol, this shows evidently that the correlation energy contribution is important in this range of angles where the hydrogen bond is not linear.

In order to see the performance of the exchange-correlation functionals considered in this work, the scan obtained with the MP2/6-311G**//HF/6-311G**, BLYP/6-311G**//HF/6-311G** and B3LYP/6-311G**//HF/6-311G** methods is presented in the Figure 3. For this case, the BLYP and B3LYP methods have essentially the same behavior each other, and regarding to the MP2 method as a reference, clearly both methods predict a higher barrier than the MP2 method, with a difference greater than 1.3 kcal/mol. It is worth to note that at 180º the MP2, BLYP and B3LYP methods predict almost the same energy (the difference is of 0.3 kcal/mol).

In the Table 2 we are reporting some PES values, single points and optimizations, for the formamide dimer at 0º, 90º and 180º with the HF/6-311G**, MP2/6-311G**, BLYP/6-311G** and B3LYP/6-311G** methods. From this table we can note that the BLYP and B3LYP energies are almost the same each other, but they are bigger than that obtained with the MP2 method for 90º, where the hydrogen bond geometrical parameters are outside the linearity, and such a difference is decreased at 180º.

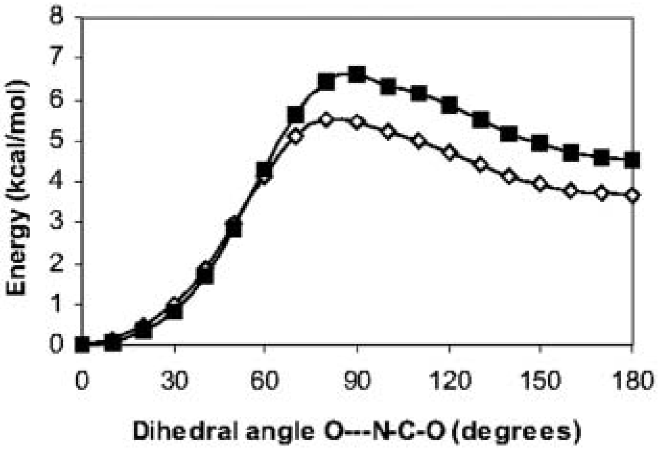

Fig. 2. Potential energy surface scan of the formamide dimer. Solid points correspond to the MP2/6-311G** method and blank points to the HF/6-311G** method.

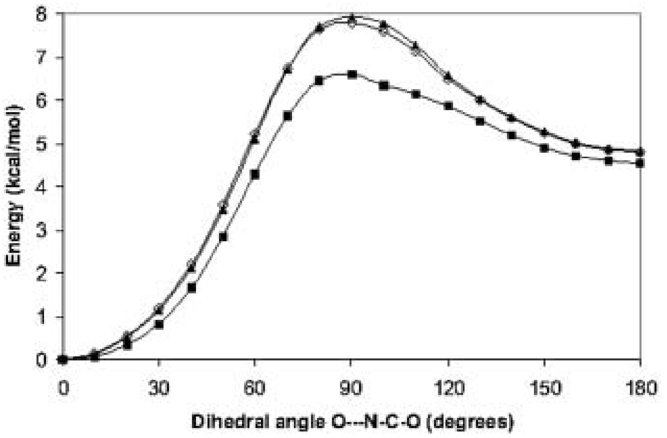

Fig. 3. Potential energy surface scan of the formamide dimer. Blank points correspond to the B3LYP/6-311G** method, solid triangles to BLYP/6-311G** method and solid squares to the MP2/6-311G** method.

Table 2. Some potential energy surface values for the formamide dimer, by changing the O---N-C-O angle. Single Point corresponds to single point calculations at the HF/6-311G** geometries and Optimized to the relaxed geometries for each method. All calculations were done with the 6-311G** basis set and the energy is reported in kcal/mol.

Method	90º	180º
	Single Point	
MP2	6.58	4.54
BLYP	7.93	4.82
B3LYP	7.78	4.80
	Optimized	
HF	5.47	3.66
MP2	6.57	4.70
BLYP	8.43	5.17
B3LYP	8.21	5.07

Table 3. Some potential energy surface values, for the formamide dimer, by changing the O---N-C-O angle. Single Point corresponds to single point calculations at the HF/cc-pVTZ geometries, and Optimized to the relaxed geometries for each method. All calculations were done with the cc-pVTZ basis set and the energy is reported in kcal/mol.

Method	80º	90º	100º	180º
		Single Point		
MP2	7.10	7.20	6.88	4.90
BLYP	6.76	7.00	6.85	4.46
B3LYP	6.85	7.02	6.80	4.50
		Optimized		
HF		5.06		3.37
MP2		7.74		5.33
BLYP		7.52		4.83
B3LYP		7.46		4.79

Additionally, to test a bigger triple-ς basis set with polarization functions, in Table 3 we are reporting some PES values by using the cc-pVTZ basis set. From this table it is impressive how the MP2 values are increased with the cc-pVTZ basis set, with regard to the 6-311G** basis set, and in a contrary behavior how the DFT values are decreased such that now they are closer to the MP2 results. This is very important result because when the hydrogen bond geometrical parameters are not favorable, MP2 and DFT would give different predictions if a limited basis set is used, as it was also observed by Ireta et al. when they applied plane waves as basis set functions [23]. Although we recognize that our study was not exhaustive to show neither the role of the basis set nor the number of the analyzed systems, we showed that a study of this type is important to finally respond in which hydrogen bonds MP2 and DFT would give different results.

Although in this work we analyzed intermolecular hydrogen bonds with the formamide dimer, this study is connected with other situation. We reported a similar behavior of nonlinear hydrogen bonds in a previous study on the alanine dipeptide, where the intramolecular N-H...O hydrogen bond is important for the stability of its conformers [24]. In that study, one of the conformers of the alanine dipeptide was described in a different way by MP2, HF and DFT in a Ramachandran plot, because the geometrical parameters of the conformer do not promote the directionality of the N-H...O hydrogen bond. In this way, the behavior observed in this work may be also mapped to intramolecular hydrogen bonds.

We should remember some points discussed in the introduction, for the *N*,*N*-dimethylformamide dimer conformers, DFT failed mainly in those dimers with a stacking conformation, where the hydrogen bond was far from linearity as in the case studied here. It suggests that the dispersion forces in these cases, as in the weak hydrogen bonds, are more important because none of the exchange-correlation functionals commonly used are able to describe systems where the dispersion forces are the relevant interaction. The contacts commanded by dispersion forces are an open field in DFT and the cases exposed here could be testing systems to future projects.

Conclusions

The results obtained in this paper show that when the hydrogen bonds geometrical parameters are distorted, common exchange-correlation functionals and MP2 give different energetic description when a limited basis set is used. It means that, even when the hydrogen bond is moderate, the prediction of these two methods will be different if the hydrogen bond is not linear. We are showing in this case that a big basis set may be used to disappear such a discrepancy, however it is necessary to make a detailed and exhaustive study of the basis set effect.

In the literature, the MP2 method is used as a reference in systems where hydrogen bonds are analyzed. However, in this work we have showed that if a limited basis set is used then the MP2 method underestimates the potential energy surface when the hydrogen bond is not linear, for DFT the contrary behavior is observed. We should remember that weak hydrogen bonds are not very linear in general, so the MP2 method may not be the best reference for this type of interactions if limited basis set functions are used. In this work, we decide to show the performance of two common exchange-correlation functionals and not functionals built ad-hoc to describe this sort of systems [25].

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