A theoretical study of hydrogen complexes of the X–H– π type between propyne and HF, HCL or HCN

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Abstract

The present manuscript reports a systematic investigation of the basis set dependence of some properties of hydrogen-bonded (π type) complexes formed by propyne and a HX molecule, where X = F, Cl and CN. The calculations have been performed at Hartree–Fock, MP2 and B3LYP levels. Geometries, H-bond energies and vibrational have been considered. The more pronounced effects on the structural parameters of the isolated molecules, as a result of complexation, are verified on $R_{C\equiv C}$ and HX bond lengths. As compared to double- ζ (6-31G**), triple- ζ (6-311G**) basis set leads to an increase of $R_{C\equiv C}$ bond distance, at all three computational levels. In the case where diffuse functions are added to both hydrogen and ‘heavy’ atoms, the effect is more pronounced. The propyne–HX structural parameters are quite similar to the corresponding parameters of acetylene–HX complexes, at all levels. The largest difference is obtained for hydrogen bond distance, R_H , with a smaller value for propyne–HX complex, indicating a stronger bond. Concerning the electronic properties, the results yield the following ordering for H-bond energies, ΔE : propyne $\cdots$ HF > propyne $\cdots$ HCl > propyne $\cdots$ HCN. It is also important to point out that the inclusion of BSSE and zero-point energies (ZPE) corrections cause significant changes on ΔE . The smaller effect of ZPE is obtained for propyne $\cdots$ HCN at HF/6-311++G** level, while the greatest difference is obtained at MP2/6-31G** level for propyne $\cdots$ HF system. Concerning the IR vibrational it was obtained that larger shift can be associated with stronger hydrogen bonds. The more pronounced effect on the normal modes of the isolated molecule after the complexation is obtained for H–X stretching frequency, which is shifted downward.

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1. Introduction

T-shaped hydrogen-bonded complexes of the type X–H– π , formed by X–H hydrogen halide and π -electron density of carbon–carbon double or triple bond, with X=Cl, F or CN, constitute very important systems since they are involved in the first step of electrophilic addition reactions to an unsaturated hydrocarbon [1]. It is well known that the complexation causes various changes in the molecular spectrum, which make such techniques suitable for characterization. Among

them are microwave and infrared molecular beam experimental techniques with Fourier transform strength [2–5]. For example, for H-bonded complexes involving acetylene and HX it is obtained an enhancement in the stretching intensities associated with chemical bonds directly involved in the H-bond formation and shifts in their vibrational frequencies [6]. Theoretical investigations using ab initio calculations have been successfully applied in order to understand the nature of the hydrogen bonding as well as changes in the structural, electronic and vibrational properties that take place in the HX and acetylene moieties after molecular complexation [7–9]. On the other hand, theoretical calculations have also been particularly useful to identify the new low-

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frequency vibrational modes that have, in general, very weak intensities.

This work reports ab initio results for hydrogen complexes involving the propyne molecule as proton acceptor and monoprotic linear acids as proton donors. One of the main tasks is to get a deeper insight into the factors controlling the formation of hydrogen-bonds, through a comparative study with the corresponding acetylene–HX complexes. Such comparison can help to get a better understanding of how the increase of the backbone alters the structural and electronic properties of unsaturated hydrogen-bonded hydrocarbons.

The choice of appropriate quantum chemistry methods and basis set in order to get a correct description of weakly bonded systems is still a difficult task. Herein, a systematic investigation using ab initio molecular orbital calculations at restricted Hartree–Fock (RHF) [10], MP2 [11], and B3LYP [12] level with several Pople basis set [13,14] have been performed. The goal is to understand the effect of electronic correlations methods and basis set size on geometrical, electronic and vibrational calculated parameters. Other important aspect is the error due the LCAO approximation; called basis set superposition error (BSSE). There are several methods to estimate the BSSE. The well-established counterpoise method developed by Boys and Bemardi [15] is chosen for the present work. The calculations were carried out using the Gaussian 98W program [16].

2. Results and discussion

2.1. Structural parameters

The select geometry parameters for the propyne···HCl, propyne···HCl and propyne···HCN optimized at Hartree–Fock, MP2 and B3LYP levels, with several basis set, are given in Table 1. An enlargement of the $R_{C\equiv C}$

bond distance is observed with the inclusion of diffuse functions in 6-31G** and 6-311G** basis set. As expected, the effect is greater for the smaller (6-31G**) basis set, at all computational levels studied. The R_{H-X} bond distance changes by few thousandths of angstroms with basis set enlargement caused by inclusion of diffusion functions. It also interesting to notice the effect due to the increase of basis set size in terms of number of functions that describes the valence electrons. It was obtained that the $R_{C\equiv C}$ bond distance increases, on average, by 0.0036, 0.0017 and 0.0073 Å at Hartree–Fock, MP2 and B3LYP levels, respectively, when the basis set increases from 6-31G** to 6-311G**, and by 0.0050, 0.0040 and 0.0077 Å when the basis set increases from 6-31++G** to 6-311++G**. As one can see, there are no significant changes in $R_{C\equiv C}$ bond distances in the propyne···HX series. Other important parameter is the H-bond distance, R_H , collected in Table 1. The effect of electron correlation on R_H is very important, and the Hartree–Fock values for R_H are higher than the corresponding values at MP2 and B3LYP levels, for all basis sets studied. The more significant effect of electronic correlation on R_H was obtained for propyne···HCl with 6-311++G** basis set, being the MP2 and B3LYP values smaller than Hartree–Fock results by 0.322 and 0.331 Å, respectively.

The most relevant geometrical parameters obtained from full geometry optimizations for propyne···HX (C_s) and acetylene···HX (C_{2v}), computed at Hartree–Fock, MP2 and B3LYP levels using 6-311++G** basis set, are shown in Fig. 1. The values in parentheses stand for the difference between the free molecule and the molecule in the hydrogen complex. As one can see, the $R_{C\equiv C}$ and R_{H-X} bond distances in propyne···HX are larger than the respective values for acetylene···HX, at all computational levels. The $R_{C\equiv C}$ bond distance in propyne···HX is higher than in acetylene···HX, on average, by 0.003 Å, being the more significant differ-

Table 1
Basis set dependence for selected geometry parameters of propyne···HX complex optimized at Hartree–Fock, MP2 and B3LYP levels

	Propyne···HCl			Propyne···HF			Propyne···HCN		
	$R_{C\equiv C}$	R_{H-Cl}	R_H	$R_{C\equiv C}$	R_{H-F}	R_H	$R_{C\equiv C}$	R_{H-C}	R_H
Hartree–Fock									
6-31G**	1.189	1.271	2.512	1.189	0.906	2.312	1.189	1.063	2.659
6-31++G**	1.191	1.271	2.595	1.192	0.908	2.318	1.191	1.063	2.724
6-311G**	1.185	1.274	2.606	1.186	0.901	2.329	1.185	1.061	2.726
6-311++G**	1.186	1.274	2.625	1.187	0.903	2.319	1.186	1.061	2.743
MP2									
6-31G**	1.222	1.278	2.290	1.222	0.929	2.165	1.221	1.070	2.432
6-31++G**	1.224	1.279	2.304	1.224	0.936	2.097	1.224	1.071	2.434
6-311G**	1.219	1.282	2.310	1.219	0.921	2.128	1.219	1.072	2.488
6-311++G**	1.220	1.282	2.303	1.220	0.926	2.099	1.220	1.073	2.468
B3LYP									
6-31G**	1.210	1.304	2.223	1.211	0.936	2.127	1.209	1.076	2.449
6-31++G**	1.212	1.302	2.281	1.212	0.942	2.076	1.211	1.077	2.508
6-311G**	1.203	1.302	2.276	1.203	0.931	2.126	1.202	1.072	2.521
6-311++G**	1.204	1.301	2.294	1.204	0.936	2.087	1.204	1.073	2.535

Fig. 1. Structural and selected geometry data for propyne...HX (C_s) and acetylene...HX (C_{2v}) complexes, computed at Hartree–Fock, MP2 and B3LYP levels using the 6-311++G** basis set.

ence obtained for propyne...HCl at B3LYP level. The R_H bond distances for propyne...HX complexes are smaller than the corresponding distance for acetylene...HX complexes, which points out to a stabilizing effect played by the CH_3 group.

2.2. H-bond energies

The basis set dependence for zero-point energies and basis set superposition error, computed at Hartree–Fock, MP2 and B3LYP levels, are shown in Table 2. The main results can be summarized as follows:

- The dependence of BSSE and ZPE values on the basis set, at Hartree–Fock and B3LYP levels, shows a similar behavior. At both levels BSSE values decrease with the increase of basis set size. However, the Hartree–Fock results for BSSE and ZPE are systematically smaller than the corresponding results at MP2 and B3LYP levels. The overestimating effect of Møller–Plesset (MP) methods on BSSE values seems to be a general trend, as shown by previous results [17].

Table 2

Zero-point energies (ΔZPE) and basis set superposition error ($\Delta BSSE$) for propyne...HX complex computed at Hartree–Fock, MP2 and B3LYP levels with various basis sets

	Propyne...HCl		Propyne...HF		Propyne...HCN	
	BSSE	ΔZPE	BSSE	ΔZPE	BSSE	ΔZPE
Hartree-Fock						
6-31G**	2.79	4.21	7.03	6.73	2.18	2.37
6-31++G**	1.25	3.74	0.67	5.87	0.60	2.16
6-311G**	1.14	3.75	4.13	6.10	1.13	2.09
6-311++G**	1.33	3.57	1.28	5.77	0.50	1.91
MP2						
6-31G**	4.20	5.21	14.84	7.78	3.97	3.75
6-31++G**	5.29	4.28	6.86	7.01	6.18	3.88
6-311G**	4.20	4.63	12.58	6.84	3.52	2.73
6-311++G**	7.26	3.60	6.63	6.29	4.83	1.71
B3LYP						
6-31G**	3.89	4.95	14.86	7.53	2.00	2.88
6-31++G**	3.62	4.48	1.10	6.19	0.89	2.61
6-311G**	1.62	4.62	11.21	6.57	1.46	2.39
6-311++G**	1.34	4.35	1.50	6.08	0.31	2.26

Values in kJ/mol.

- (ii) The highest values for BSSE were obtained at MP2 and B3LYP levels with 6-31G** and 6-311G** basis set for the propyne···HF hydrogen complex. In addition, the effect represented by the inclusion of diffuse functions, on BSSE values, is more pronounced for such complex, at MP2 and B3LYP levels. For example, at B3LYP level the BSSE decrease by 13.76 and 9.71 kJ/mol when the basis set changes from 6-31G** to 6-31++G** and from 6-311G** to 6-311++G**, respectively.

The results for H-bond stabilization energies (ΔE), with and without inclusion of zero-point and BSSE correction (ΔE^{CORR}), obtained at Hartree–Fock, MP2 and B3LYP levels using various basis sets are collected in Table 3. As one can observe, the results for ΔE , at Hartree–Fock level, are systematically smaller than the MP2 and B3LYP results. As long as diffuse functions are included, the effect of increasing the basis set size from double- to triple- ζ is small, at all computational levels. On the other hand, the inclusion of diffusion functions causes a significant decrease in ΔE . At B3LYP level, for instance, ΔE decreases by 8.9 kJ/mol, from 6-31G** to 6-31++G**, for propyne···HF system. Considering the Hartree–Fock results for ΔE , the ordering of the stabilization energy is: propyne···HF > propyne···HCl $\sim$ propyne···HCN. However, at B3LYP and MP2 levels the difference between ΔE values obtained for propyne···HCl and propyne···HCN becomes more pronounced, with propyne···HCl > propyne···HCN. The inclusion of BSSE and ZPE energies corrections causes significant changes on ΔE . The smallest effect due to such factors is obtained for propyne···HCN at HF/6-311++G** level, with a difference of 2.40 kJ/mol between ΔE and ΔE^{CORR} . The greatest effect is in turn observed for propyne···HF system at MP2/6-31G** level, with a corresponding energy difference of 22.62 kJ/mol.

Table 3

Basis set dependence of H-bond energies (ΔE) and H-bond energies including zero-point and BSSE corrections (ΔE^{CORR}) for propyne···HX complex computed at Hartree–Fock, MP2 and B3LYP levels

	Propyne···HCl		Propyne···HF		Propyne···HCN	
	ΔE	ΔE^{CORR}	ΔE	ΔE^{CORR}	ΔE	ΔE^{CORR}
Hartree–Fock						
6-31G**	11.83	4.84	20.87	7.10	11.70	7.14
6-31++G**	9.03	4.04	15.90	9.37		
6-311G**	9.62	4.73	18.92	8.69	9.74	6.53
6-311++G**	8.99	4.08	15.96	8.91	8.73	6.33
MP2						
6-31G**	18.42	9.00	28.64	6.02	16.53	8.81
6-31++G**	18.28	8.72	24.78	10.90	16.13	6.06
6-311G**	16.02	7.20	26.48	7.07	14.12	7.87
6-311++G**	18.46	7.60	24.00	11.08	15.41	8.82
B3LYP						
6-31G**	19.12	10.27	32.45	10.06	14.99	10.11
6-31++G**	14.38	6.28	23.55	16.26	10.87	7.36
6-311G**	15.10	8.86	28.88	11.11	11.43	7.58
6-311++G**	13.78	8.09	22.98	15.39	9.94	7.37

Values in kJ/mol.

Fig. 2. Stabilization energies, ΔE (kJ/mol), for propyne···HX (C_8) and acetylene···HX (C_{2v}) complexes, computed at Hartree–Fock, MP2 and B3LYP levels using the 6-311++G** basis set.

A comparison between H-bond energies of acetylene···HX and propyne···HX systems is shown in Fig. 2. The propyne···HX hydrogen complexes are more stable than its analogous acetylene complex. The H-bond energy is higher by 3.59, 5.55 and 5.08 kJ/mol, at Hartree–Fock, MP2 and B3LYP levels (with 6-311++G** basis set), respectively. In the case where HCN is the proton donor, the stabilizing effect of the additional methyl group is smaller, leading to H-bond energies differences of 1.93, 3.87 and 2.61 kJ/mol at Hartree–Fock, MP2 and B3LYP levels, respectively. In a similar way, it was obtained that the propyne···HCl complex is more stable than the respective acetylene complex by 2.23, 5.27 and 3.79 kJ/mol. These trends are in agreement with the results obtained for R_H , for R_H values obtained for propyne···HX systems are smaller than the ones obtained for the corresponding acetylene···HX complexes.

2.3. Vibrational properties

As aforementioned, the formation of H-bond produces several changes in the vibrational spectrum of the molecule after the complexation. Table 4 shows the basis set dependence for harmonic frequency shifts, $\nu_{\text{HX}}^{\text{str,C}} - \nu_{\text{HX}}^{\text{str}}$, that is, the frequency difference between the H–X stretching mode in the complex and in the free molecule, as well as the H–X stretching intensities ratios upon H-bond formation. The H–X stretching frequency is shifted downward after the complexation in all propyne···HX complexes. The stretching frequency shifts obtained from Hartree–Fock method are systematically smaller than the ones from MP2 and B3LYP methods. One should keep in mind at this point that harmonic approximation is used in order to evaluate the vibrational properties. However, it is not so easy to speculate about the anharmonic effects on zero-point energies and frequency modes. Nevertheless, as can be seen from Table 3, there is a fair dependence of the harmonic frequency shifts on the basis set, with maximum value of $\approx 81 \text{ cm}^{-1}$ for propyne···HF at

Table 4

Basis set dependence of harmonic frequency shifts ($\nu_{\text{HX}}^{\text{str,C}} - \nu_{\text{HX}}^{\text{str}}$) in cm^{-1} , and infrared intensities ratios after complexation ($A_{\text{HX}}^{\text{str,C}}/A_{\text{HX}}^{\text{str}}$), for HX stretching

	Propyne...HCl		Propyne...HF		Propyne...HCN	
	$\nu_{\text{HCl}}^{\text{str,C}} - \nu_{\text{HCl}}^{\text{str}}$	$A_{\text{HCl}}^{\text{str,C}}/A_{\text{HCl}}^{\text{str}}$	$\nu_{\text{HF}}^{\text{str,C}} - \nu_{\text{HF}}^{\text{str}}$	$A_{\text{HF}}^{\text{str,C}}/A_{\text{HF}}^{\text{str}}$	$\nu_{\text{HC}}^{\text{str,C}} - \nu_{\text{HC}}^{\text{str}}$	$A_{\text{HC}}^{\text{str,C}}/A_{\text{HC}}^{\text{str}}$
Hartree–Fock						
6-31G**	–83	7.9	–117	2.7	–51	2.7
6-31++G**	–65	5.9	–143	3.1	–45	2.5
6-311G**	–62	4.6	–121	2.6	–42	2.3
6-311++G**	–61	4.5	–146	3.0	–42	2.4
MP2						
6-31G**	–132	16.1	–158	4.0	–75	3.9
6-31++G**	–125	13.9	–236	5.2	–75	3.8
6-311G**	–128	10.2	–177	4.1	–73	3.1
6-311++G**	–128	10.3	–227	4.8	–	–
B3LYP						
6-31G**	–242	34.9	–230	6.5	–108	5.2
6-31++G**	–209	27.5	–325	7.2	–96	4.5
6-311G**	–209	18.4	–374	9.0	–89	4.0
6-311++G**	–196	17.8	–311	6.4	–89	4.0

MP2 level as the basis set increases from 6-31++G** to 6-311++G**.

The larger shifts can be associated with stronger hydrogen bonds. At Hartree–Fock and MP2 levels the ordering obtained for frequency shifts is: propyne...HF > propyne...HCl > propyne...HCN, which is the same ordering obtained for the H-bond stabilization energies showed in Table 3. However, at B3LYP level (with the 6-31G** basis set) the frequency shift for propyne...HCl is greater than for propyne...HF, which is in agreement with the ΔE^{CORR} showed in Table 3.

The Hartree–Fock results for IR intensities of the proton donor are less affected by complexation than the MP2 and B3LYP values, with the greatest ratio of $A_{\text{HX}}^{\text{str,C}}/A_{\text{HX}}^{\text{str}}$ amounting to 7.9 (see Table 4). The corresponding MP2 and B3LYP values vary from 10.2 to 34.9. The ordering, at all computational levels, is: propyne...HCl > propyne...HF $\approx$ propyne...HCN.

3. Conclusions

The basis set dependence of some electronic and structural properties of X–H- π type hydrogen complexes formed between propyne and HF, HCl and HCN have been studied at Hartree–Fock, MP2 and B3LYP levels. The stabilization energies, ΔE , as well as the corrected stabilization energies, ΔE^{CORR} , which includes the BSSE and ZPE corrections, computed at Hartree–Fock and B3LYP levels, show that the BSSE results decrease with the basis set size. However, the Hartree–Fock values of ΔE , BSSE and ZPE are systematically smaller than the corresponding values at MP2 and B3LYP levels. Previous results yield that the BSSE is in general overestimated by Møller–Plesset (MP) methods. Considering the results for ΔE at Hartree–Fock level, the ordering obtained for the stabilization energy is:

propyne...HF > propyne...HCl $\sim$ propyne...HCN. However, the B3LYP and MP2 results for ΔE lead to a greater energy difference between the complexes with HCl and HCN, where propyne...HF > propyne...HCl > propyne...HCN. The BSSE and ZPE corrections cause significant changes on ΔE . Another important result is that the hydrogen bond of the propyne...HX complex is more stable than the one of the acetylene...HX system. For example, the H-bond energy of propyne...HF is higher than the one of acetylene...HF by 3.59, 5.55 and 5.08 kJ/mol at Hartree–Fock, MP2 and B3LYP levels, respectively, with the 6-311++G** basis set. On the other hand, the propyne...HCN hydrogen complex is more stable than the acetylene...HCN system by 1.93, 3.87 and 2.61 kJ/mol at Hartree–Fock, MP2 and B3LYP levels, respectively. Similarly, it has been obtained that the propyne...HCl complex is more stable than the respective acetylene complex by 2.23, 5.27 and 3.79 kJ/mol.

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