Chemical Physics xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Hydrogen bonding between hydrides of the upper-right part of the periodic table

Matjaž Simončič, Tomaz Urbic *

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:
Received 20 January 2018
In final form 29 March 2018
Available online xxxx

ABSTRACT

One of the most important electrostatic interactions between molecules is most definitely the hydrogen bond. Understanding the basis of this interaction may offer us the insight needed to understand its effect on the macroscopic scale. Hydrogen bonding is for example the reason for anomalous properties in compounds like water and naturally life as we know it. The strength of the bond depends on numerous factors, among them the electronegativity of participating atoms. In this work we calculated the strength of hydrogen bonds between hydrides of the upper-right part of the periodic table (C, N, O, F, P, S, Cl, As, Se, Br) using quantum-chemical methods. The aim was to determine what influences the strength of strong and weak hydrogen bonds in simple hydrides. Various relationships were checked. A relation between the strength of the bond and the electronegativity of the participating atoms was found. We also observed a correlation between the strength of hydrogen bonds and the inter-atomic distances, along with the dependence on the charge transfer on the atom of the donor. We also report characteristic geometries of different dimers.

1. Introduction

The hydrogen bond is the strongest intermolecular interaction. Its main constituent is the electrostatic attraction force between two polar groups which occurs when a molecule with a hydrogen atom bonded to an electronegative atom donates the hydrogen to another electronegative element, but it is expected that there are also quantum effects involved. The hydrogen bond interaction is also of paramount importance for the development of life on Earth as we know it. It plays a major role in the formation of Watson-Crick base pairs in the DNA and RNA molecules [1–6] and it is important in protein structures as an interaction between parts of proteins and between proteins and water molecules [7]. Hydrogen bonds are also the main reason for anomalous properties in the most important substance on our planet, namely water. It is known that water has more than 70 anomalous properties [8–10]. For instance, water has a density maximum at 4 °C, an unusually high specific heat capacity, a boiling point at 100 °C (p = 1 atm) whereas all the other hydride analogues have sub-zero boiling points [11] etc. Such anomalies are not limited only to the oxygen hydride, since HF and NH_3 also exhibit similar behaviour, moreover hydrogen bonds appear between other hydrides of the examined part of the periodic table. For a better understanding of this interaction the point of interest is knowing the strength of the hydrogen bond and its correlations with other properties.

A thorough research regarding the hydrogen bond in a larger extend was done by Scheiner [12], who described the theoretical background of hydrogen bonding (strength of the HB, equilibrium geometries etc.). The strength of the HB depends on numerous factors including the intermolecular distances, the relative orientation of both molecules and also on the local environment [13]. Hydrogen bonding also enables cluster formation, which is most commonly observed with water molecules [14–21]. For example, the water dimer can form six additional hydrogen bonds thus creating the first coordination shell. In calculations this can be considered as local environment and studies have shown that even the second coordination shell around a water-water dimer can have a non-negligible effect on the strength of the hydrogen bond [13,22]. Experimentally determined data considering the water dimer was also obtained, for instance the binding energy for the most commonly studied water-water dimer in the gaseous phase was obtained by studying the thermal conductivity of the H_2O and D_2O vapours [23]. Similar theoretical and experimental research has been done with clusters of only alcohol [24–26] or alcohol-water mixtures [27–30], whereas some of the research also focused on HF, HF-water clusters [31,32] and even aromatic alcohol-water clusters [33].

The HB occurs between hydrides of the second row [34] although the emphases is on the $(H_2O)_2$ and the $(NH_3)_2$ dimer

* Corresponding author.
E-mail address: tomaz.urbic@fkkt.uni-lj.si (T. Urbic).

https://doi.org/10.1016/j.chemphys.2018.03.036
0301-0104/

[35–37]. The ammonia dimer being of particular interest because of its multiple equilibrium geometry structures. Integrating the theoretical knowledge of those dimers opened the gateway to the thermodynamic evaluation of the hydration of the ammonium ion [38,39], which plays a key role in biological systems.

Unknown to many, the HB occurrence extends also to the region of the third and forth row hydrides. With the use of *ab initio* calculations and experimental analysis (molecular beam microwave spectroscopy, IR matrix isolation spectroscopy, and IR spectroscopy in conventional and cryosolutions) Sennikov [40,41] provided an overview of weak hydrogen bonding by third row (PH_3, H_2S) and fourth row (AsH_3, H_2Se) hydrides, deepening our understanding of the HB with practical applications – chemical vapor deposition (CVD) for the production of thin semiconductor films. The C-H···X hydrogen bonds are weaker bonds which are still being studied and are not yet well understood but are believed to contribute to the structure of biomolecules [42]. Because of the importance which the hydrogen bond holds in everyday life, other hydrogen bonded analogues have been evaluated, for example the HCN···CHN and HCN···HF dimers [43], whilst others studied the mechanism of hydrogen bonding and found similarities with the halogen bond [44]. Such evaluations were expanded upon from simple hydrides to more complex organic compounds [45–47]. Accurate bonding energies between hydrocarbons and water are essential for predictions of stabilities of such systems. Unfortunately the binding energy of those is hard to measure experimentally, so quantum–mechanical calculations are used and consequently exploited for the study of methane clathrates. For example the work of Pal and Kundu focuses on the effect the methanol molecule has on the formation of the methane hydrate cage [48]. Such calculations are also beneficial for the successful prediction of phase diagrams in the region where methane hydrates form [49,50].

The goal of this contribution is to find correlations between the strength of the HB and other properties in connection with hydrogen bonding (interatomic distances, angles, charge transfers, electronegativity etc.) in most simple systems – hydrides of electronegative elements. Although some calculations already exist, we extended the calculations of the HB towards compounds containing less electronegative atoms, like arsenic, selenium and phosphorus. Consequently the aim of this paper is also the attempted generalization of the characteristics of simple hydrogen bonded compounds (for weaker and stronger hydrogen bonds). The following was done by calculating the energies of simple clusters consisting of pairs of two molecules ($HF\cdots HCl$,$NH_3\cdots HBr$*etc.*), using a post Hartree-Fock calculation. As an important factor when considering the strength of the HB one must take the temperature and pressure into account as considered by Dougherty and Howard [51], however the emphasis of this paper are the correlations between the aforementioned characteristics of the HB thus the temperature-pressure dependence has not been considered.

2. Methods and discussion

We have calculated the strength of hydrogen bonds in dimers of compounds where the hydrogen atom is bound to a more electronegative atom (HF, HCl, HBr, H_2O, H_2S, H_2Se, NH_3, PH_3, AsH_3 and CH_4), altogether 90 different dimers, using the Gaussian 09 [52] program suite, employing MP2 (full) method [53] with the Aug-CC-pVTZ basis set [54] both with and without basis set superposition error (BSSE). Equilibrium geometries of the monomers along with net charges of the constituent atoms are listed in Table 1 and dimers in Table 2. After the energy minimization of the dimers, we calculated the hydrogen bond interaction energy by subtracting the energy of the optimized individual monomers from the energy of the optimized dimers. After that we checked possible correlations between the strength of the interaction and the electronegativity of the participating atoms as well as geometries (angles and inter-atomic distances), generated electric field and electron transfer (the charges on the individual atoms, which were obtained via the Mulliken population analysis).

Table 1
Geometries (distance and angles) of hydride monomers along with the net charges on the constituent atoms. Distances are in Ångströms, the HXH angles in degrees.

Monomer	r_{XH}	∠HXH	e_X	e_H	Geometry
HF	0.920	/	−0.377	0.377	
HCl	1.271	/	−0.200	0.200	
HBr	1.399	/	−0.025	0.025	
H_2O	0.959	104.27	−0.441	0.220	
H_2S	1.332	91.97	−0.342	0.171	
H_2Se	1.443	90.71	0.168	−0.084	
NH_3	1.009	107.04	−0.595	0.198	
PH_3	1.407	92.99	−0.275	0.092	
AsH_3	1.489	91.70	0.470	−0.157	
CH_4	1.084	109.47	−1.192	0.298	

We tested the correctness of our quantum chemical method by firstly making the calculation and full geometry optimization of the water monomer with the aforementioned method and basis set which yielded the OH bond length of 0.9588 Åand the HOH angle 104.27° which is close to the experimentally determined values (0.9572 Åand 104.52°) [55] for the isolated water molecule in a vacuum. We continued with the geometry optimization of the water-water dimer using the same method and basis set, for which the oxygen–oxygen distance was 2.888 Å, which is close to the experimentally determined value by Odutola and Dyke [56], 2.946 Å. The hydrogen bond interaction energy in the water dimer is -4.68 kcal mol^{-1}, being in agreement with the commonly quoted empirical value which is -5.4 ± 0.7 kcal mol^{-1} [57,58]. Our calculations are also in good agreement with the calculations performed by other authors [59–62].

Geometry optimizations were performed on all monomers and 90 different dimers, pairs of two molecules (see above) where each monomer can act as a donor and as an acceptor of hydrogen except for CH_4 which can only act as a donor. For convenience sake we shall depict the hydrogen bond in this format: X-H···Y. We completed the energy minimization using two different procedures. Most of the equilibrium geometries were obtained through the direct optimization, whereas some were acquired using the