

This manuscript (type – report) concerns the new definition of hydrogen bonding interaction. Additionally few explanations, footnotes and suggestions are included, namely, this short manuscript consists of the following parts:

1. Definition of hydrogen bonding,
2. List of criteria,
3. Some characteristics of hydrogen bonds
4. Footnotes which are referred to some parts of the previous sections.

Generally such an article is probably needed since the hydrogen bonding interaction is often the subject of investigations. Numerous kinds of new interactions are analyzed recently and investigators do not know which of them classify as hydrogen bonds and which are not. On the other side, because of the numerous interactions which exist in gas, liquid and solid state and which differ sometimes only slightly between themselves the useful definition is very hard to construct.

In my opinion the study is valuable but let me present numerous doubts and reservations.

The definition (lines 3-6) practically does not differ significantly from that one given by Pimentel and McClellan (Pimentel, G.C.; McClellan, A.L. *The Hydrogen Bond*, W.H. Freeman and Company, San Francisco and London, **1960**, page 6), even the sequence “there is evidence of bond formation” occurs in the monograph of Pimentel and McClellan and also in this study. And the latter statement is the main weakness of both definitions since what does it mean “evidence of bond formation”. This is not any well defined physical term. The new and important statement of this new definition is that X-H occurs “in which X is more electronegative than H”. However, in such a way, the hydrogen bonding is defined by the other term “electronegativity” which is also the subject of numerous definitions and controversies. What is also very important – how could somebody know if X is more electronegative than H, approximately from the Pauling scale, or any other scale. Of course, electronegativities of the same atoms change, it depends on compound, environment etc. Thus maybe atomic charges should be considered as those expressing electronegativities. Again – charges are not experimentally measurable quantities and if calculated - they depend on the population analysis applied. Intuitively someone expect H-bonds for such arrangements as O-H...O, N-H...O, even C-H...O but not for all C-H...Y systems, thus if there were any

doubts if any interaction should be classified as hydrogen bond thus it still remains after the use of the definition proposed.

The use of the term X-H in the definition suggests that one of interactions for X-H...Y arrangement is the covalent bond (less or more polarized). However the question arises if so-called proton bound homodimers should be classified as hydrogen bonds (B.Chan, J.E.Del Bene, *Molecular Physics* 107 (2009) 1095.). $\text{H}^+(\text{nitrobenzene})_2$ is an example (D.Stasko, S.P.Hoffmann, K-C.Kim, N.L.P.Fackler, A.S.Larsen, T.Drovetskaya, F.S.Tham, C.A.Reed, C.E.F.Rickard, P.D.W.Boyd, E.S.Stoyanov, *J.Am.Chem.Soc.* 124 (2002) 13869.) but there are also the other simple complexes like $\text{H}_2\text{O}\dots\text{H}_3\text{O}^+$, $\text{NH}_4^+\dots\text{NH}_3$ and related ones where the proton is situated in the mid-point of X...X distance or nearly so (Y.Kita, T.Udagawa, M.Tachikawa, *Chemistry Letters* 38 (2009) 1156. – It is an interesting study on such simple complexes).

These above reservations concern the body of the definition, how it could be applied to classify interactions analyzed.

There are the other parts of this study which are controversial in my opinion.

The authors write that "acceptor is an electron rich region such as a lone pair or a π cloud" - for multicenter proton acceptors. What about σ -bonds and the systems like $\text{NH}_4^+\dots\text{H}_2$ (Urban, J.; Roszak, S.; Leszczynski, J. *Chem.Phys.Lett.* **2001**, 346, 512.) For such a system the binding energy is not negligible and the dispersive forces are not most important attractive ones! Besides H_2 molecule elongates and loses electron charge after complexation, thus acts as Lewis base.

Lines 22-25, The forces involved in H-bond formation are given: "electrostatic", "charge transfer", "dispersion" (briefly speaking). These terms are commonly known and defined by various decomposition schemes. However, what does it mean "responsible for the formation of a partial covalent bond" - aren't they those attributed as charge transfer?

F2 "If an interaction is primarily due to dispersive forces, then it would not be characterized as a hydrogen bond" - why not? Lines 22-25 present different interaction energy terms derived from decomposition scheme, also dispersive, why this kind of attractive interaction is worse than the other ones, besides: what does it mean "primarily due to dispersive forces" - it is the open door to speculations which

decomposition shows such an effect, what is primarily (greater than other attractive terms?), which decomposition is the proper tool, etc. Besides, if the dominance of dispersive forces qualify any interaction as non-hydrogen bonding thus it should be included in the definition?

F4 – the hydrogen bond angle tends toward 180° and should preferably be value above 110 (why not 109 or 111, it is not the strong point to give the arbitrary value). The angle dependence “the stronger the hydrogen bond, the more linear is X-H...Y angle ...”, it should be applied to ranges, as it was pointed out by Desiraju and Steiner (Desiraju, G.R.; Steiner T. *The weak hydrogen bond in structural chemistry and biology*; Oxford University Press Inc., New York, **1999**). Approximately, it was stated that for very strong hydrogen bonds the A-H...B angle range is $175-180^\circ$, for strong it is $130-180^\circ$ while for weak $90-180^\circ$.

I think that the list of criteria was not correctly constructed and the same concerns characteristics of hydrogen bonds.

Few examples:

- (in characteristics) “Hydrogen bonds are involved in proton transfer reactions” - it is not common, numerous hydrogen bonds are not involved (the discussion included in the following study is interesting: Alkorta, I.; Rozas, I.; M \acute{o} , O.; Y \acute{a} ñez, Elguero, J. *J.Phys.Chem.A* **2001**, *105*, 7481.),
- Line 61, “the interaction energy correlates well with the extent of charge transfer between the donor and the acceptor” - I agree that there is such good correlation if the charge transfer energy is considered, but in the case of charges calculated it is usually not good,

Line 65, the bond path is not an indicator of the existence of hydrogen bonding, BPs show the favorable interactions for the structure being in energetic minimum (R.F.W.Bader, *J.Phys.Chem. A* 1998, *102*, 7314-7323.; R.F.W.Bader, *J.Phys.Chem. A* 2009, *113*, 10391-10396.). There are numerous species where BPs were not found and the interactions could be classified as hydrogen bonds and reverse, BPs exist but no hydrogen bonds.

Of course the authors write “some criteria and characteristics for hydrogen bonding, not necessarily exclusive... the greater the number of criteria satisfied, the more reliable

is the characterization as a hydrogen bonds". However the greater number of them listed in this study is problematic.

At the end, I would like to write that the above reservations are not pointed out to show that this study or the definition of hydrogen bonding is not useful. The authors collected numerous observations on hydrogen bonding, its characteristics etc. which are the subject of various studies. That is why the definition and the comments included would be useful for others. However I have got doubts to apply these statements by others who work on various interactions, also hydrogen bonding. How could the presented definition be useful?