

The recommendation for a “Definition of The Hydrogen Bond” is a valuable enterprise. The document submitted to Div I on January 15, 2010 not only contains important elements contributing to that, it also shows the substantial work needed to achieve such a task. However, I would like to address the following comments to the authors and to further consideration by Division I.

#### 1. General remarks

The definition of the H-bond is quite a difficult task, indeed. It is my impression that a short definition, that is simultaneously pregnant and flexible, should somewhat be preferred over longer definitions that enlist several criteria which will not find the agreement of all.

I quote from one of the author's article (Goswami and Arunan, PCCP, 11,8974 (2009)):

“Finally, the definition given by Pimentel and McClellan” - G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond', Freeman and Co, San Francisco, 1960 - “appears to be the most appropriate for a hydrogen bond. According to them, 'A hydrogen bond is said to exist when: (1) there is evidence of a bond and (2) there is evidence that this bond specifically involves a hydrogen atom already bonded to another atom.' “

I understand that under (1) Pimentel and McClellan mean “chemical” bond (thus covalent bond), and under (2) they mean a three-body covalent bond.

If this is so simply said, why not just take this definition?

I am afraid, that the presently proposed document will generate quite some (negative) impact in the physical and chemical community. Stating, in particular, that X be more electronegative than H is a rather restrictive point. The (BH<sub>3</sub>)-dimer would not fall under H-bonded complexes, which would surprise, I guess. Besides, would this definition not depend on the electronegativity scale used? I also think that the covalent nature of the H-Bond is somewhat too much hidden in criterion (1).

#### 2. Specific remarks

Page 1, line 7 outer line numbering column, write rather: “The hydrogen bond results from an attractive interaction between ..”

Page 1, line 34: Is there a hierarchy in this list? If yes, the order should be (2), (3), (6), (1), (4), (5)

Page 2, line 35: The letter “p” in pK must be written in upright roman style.

Page 2, line 41: “(2) Hydrogen bonds may be involved in proton transfer reactions.”

Page 3, lines 7 and 8: This text is not widely understandable. Either extend explanations considerably, or delete.

Page 3, line 19: “donor/acceptor” is unclear; do the authors mean the “donor-acceptor pair”?

Page 3, line 53: The HF-dimer is not linear (Quack and Suhm JCP 95, 28 (1991)). There are examples that are in contradiction with the statements given in this text; e.g. H<sub>2</sub>O—HF (non-linear, although strong); or H<sub>2</sub>S—HF, which is at about 90°: is this complex not H-bonded?

Page 4, line 34ff: The concept of thermal energy along a vibrational coordinate is difficult to accept. This quantity cannot be measured, and it is difficult to calculate, since vibrational coordinates are generally coupled (sometimes even strongly in H-bond complexes). Furthermore, there is a problem with the thermal stability criterion: (H<sub>2</sub>O)<sub>2</sub> is thermally stable with respect to the monomers (the reaction enthalpy for 2H<sub>2</sub>O = (H<sub>2</sub>O)<sub>2</sub> is -22.4 kJ/mol at 300K), but is not observed, because of entropy (the corresponding reaction Gibbs energy is 15.4 kJ/mol, at 300K).

Page 4, line 53, write rather: “.. is often determined by the principle of close-packing..”, since benzene is an example.

Prof. R. Marquardt. Strasbourg, March 26, 2009.