Definition of the hydrogen bond (IUPAC Recommendations 2011)*

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Abstract: A novel definition for the hydrogen bond is recommended here. It takes into account the theoretical and experimental knowledge acquired over the past century. This definition insists on some evidence. Six criteria are listed that could be used as evidence for the presence of a hydrogen bond.

Keywords: bonding; charge transfer; hydrogen bond; IUPAC Physical and Biophysical Chemistry Division; molecular interactions; noncovalent interactions.

1. PREAMBLE

The task group recommends the definition given here for the hydrogen bond. The short definition is followed by a list of experimental and/or theoretical criteria, which can be used as evidence for the presence of the hydrogen bond. Finally, some characteristics that are typical of hydrogen-bonded systems

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are given. A brief explanation of the terms used is provided after the definition. Moreover, several foot-notes (indicated by F#) have been added, and these are given at the end. These footnotes are intended to give more explanation for the sake of clarity and completeness. The task group has also produced a comprehensive technical report, which appears elsewhere in this issue of *Pure and Applied Chem*istry [1]. This report provides a summary of the past work on hydrogen bonding and also the rationale for the proposed definition.

2. DEFINITION

The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.

A typical hydrogen bond may be depicted as X–H$\cdots$Y–Z, where the three dots denote the bond. X–H represents the hydrogen bond donor. The acceptor may be an atom or an anion Y, or a fragment or a molecule Y–Z, where Y is bonded to Z. In some cases, X and Y are the same. In more specific cases, X and Y are the same and X–H and Y–H distances are the same as well leading to symmetric hydrogen bonds. In any event, the acceptor is an electron rich region such as, but not limited to, a lone pair of Y or π-bonded pair of Y–Z.

The evidence for hydrogen bond formation may be experimental or theoretical, or ideally, a combination of both. Some criteria useful as evidence and some typical characteristics for hydrogen bonding, not necessarily exclusive, are listed below, numbered E# and C#, respectively.[F1] The greater the number of criteria satisfied, the more reliable is the characterization as a hydrogen bond.

2. 1 List of criteria

For a hydrogen bond X–H$\cdots$Y–Z:

(E1) The forces involved in the formation of a hydrogen bond include those of an electrostatic origin,[F2] those arising from charge transfer between the donor and acceptor leading to partial covalent bond formation between H and Y, and those originating from dispersion.

(E2) The atoms X and H are covalently bonded to one another and the X–H bond is polarized, the H$\cdots$Y bond strength increasing with the increase in electronegativity of X.[F3]

(E3) The X–H$\cdots$Y angle is usually linear (180º) and the closer the angle is to 180º, the stronger is the hydrogen bond[F4] and the shorter is the H$\cdots$Y distance.[F5]

(E4) The length of the X–H bond usually increases on hydrogen bond formation leading to a red shift in the infrared X–H stretching frequency and an increase in the infrared absorption cross-section for the X–H stretching vibration. The greater the lengthening of the X–H bond in X–H$\cdots$Y, the stronger is the H$\cdots$Y bond. Simultaneously, new vibrational modes associated with the formation of the H$\cdots$Y bond are generated.[F6]

(E5) The X–H$\cdots$Y–Z hydrogen bond leads to characteristic NMR signatures that typically include pronounced proton deshielding for H in X–H, through hydrogen bond spin–spin couplings between X and Y, and nuclear Overhauser enhancements.

(E6) The Gibbs energy of formation for the hydrogen bond should be greater than the thermal energy of the system for the hydrogen bond to be detected experimentally.[F7]

2.2 Some characteristics of hydrogen bonds

(C1) The pK_a of X–H and pK_b of Y–Z in a given solvent correlate strongly with the energy of the hydrogen bond formed between them.

(C2) Hydrogen bonds are involved in proton-transfer reactions (X–H···Y → X···H–Y) and may be considered the partially activated precursors to such reactions.

(C3) Networks of hydrogen bonds can show the phenomenon of co-operativity, leading to deviations from pair-wise additivity in hydrogen bond properties.

(C4) Hydrogen bonds show directional preferences and influence packing modes in crystal structures.[F8]

(C5) Estimates of charge transfer in hydrogen bonds show that the interaction energy correlates well with the extent of charge transfer between the donor and the acceptor.

(C6) Analysis of the electron density topology of hydrogen-bonded systems usually shows a bond path connecting H and Y and a (3,–1) bond critical point between H and Y.[F9]

2. 3 Footnotes

F1. It is understood that there will be borderline cases for which the interpretation of the evidence might be subjective. In any case, there should be no gross deviations from the above-mentioned criteria. With further progress in experimental and theoretical methods, new criteria for hydrogen bonding could evolve. It may be noted that a given donor or acceptor may form hydrogen bonds with more than one acceptor or donor, respectively, in a hydrogen-bonded network. When such multiple interactions are present, some of the correlations given above may not follow. Moreover, the correlations work better when the donor or acceptor is fixed while varying acceptors or donors.

F2. Attractive interactions arise from electrostatic forces between permanent multipoles, inductive forces between permanent and induced multipoles, and London dispersion forces. If an interaction is primarily due to dispersion forces, then it would not be characterized as a hydrogen bond. Thus, neither $Ar \cdots CH_4$ nor $CH_4 \cdots CH_4$ are hydrogen-bonded systems. The importance of various components of hydrogen bonding may vary quite widely from system to system.

F3. It should be remembered that the electronegativity of the elements could change depending on the chemical environment. This is particularly true of organometallic and other highly polarizable systems. However, it is recommended that no system in which H does not carry a partial positive charge in X–H···Y be considered as hydrogen bonded.

F4. The X–H···Y hydrogen bond angle tends toward 180º and should preferably be above 110º. For example, the hydrogen fluoride dimer is nearly linear and is a hydrogen-bonded system. However, the lithium fluoride dimer has both LiF molecules oriented anti-parallel because of strong dipole–dipole interactions and would not be considered as being (analogously) lithium bonded.

F5. Historically, the X to Y distance was found to be less than the sum of the van der Waals radii of X and Y, and this shortening of the distance was taken as an infallible indicator of hydrogen bonding. However, this empirical observation is true only for strong hydrogen bonds. This criterion is not recommended. In most cases, the distance between H and Y are found to be less than the sum of their van der Waals radii. It should be noted that the experimental distances are vibrational averages and would differ from such distances calculated from potential energy minimization.

F6. In general, for the donor, the X–H bond length increases and there is an associated red shift in the X–H stretching frequency. There are, however, certain hydrogen bonds in which the X–H bond length decreases and a blue shift in the X–H stretching frequency is observed. It is conceivable that a hydrogen bond could exist without a red or a blue shift. To a lesser extent, in the acceptor, the Y–Z bond deviates from the length of the Y–Z bond in the isolated subunit. The Y–Z bond vibrational frequencies and spectral band intensities also show corresponding changes on hydrogen bond formation.

F7. For hydrogen bonding to have any practical significance, it should be thermally stable. Hence, a hydrogen-bonded complex, between donor and acceptor molecules, produced in a supersonic beam or a cryogenic matrix, may not be found in a room temperature mixture of the two mole-

cules. Moreover, the thermal energy along vibrational coordinates that can destroy the orientational preference should be less than the barrier along those coordinates. This explains why H_2S has 12 neighbors and is not hydrogen bonded when it freezes at –60 °C but shows features of hydrogen bonding at much lower temperatures.

F8. Hydrogen bonds are directional and influence crystal packing modes in chemically understandable ways. The crystal packing of a non-hydrogen-bonded solid (say, naphthalene) is often determined by the principle of close-packing, and each molecule is surrounded by a maximum number of other molecules. In hydrogen-bonded solids, there are deviations from this principle to a greater or lesser extent depending upon the strengths of the hydrogen bonds that are involved. Correspondingly, the hydrogen bond geometries are conserved with fidelities that depend on their strengths.

F9. Critical points in electron density topology refer to the points where the electron density is an extremum, i.e., a minimum or a maximum. The first derivative of electron density is zero in these points, and the second derivative would be positive for a minimum and negative for a maximum. A (3,–1) critical point implies that the electron density is an extremum in all three directions leading to the first digit in parenthesis, 3. The second digit is obtained by adding 1 for directions in which the electron density is minimum and –1 for directions in which the electron density is maximum. A (3,–1) critical point is usually found between two atoms that are bonded, i.e., along the bond between the two atoms the electron density is a minimum at this point and in the two directions away from the bond, it is maximum, thus leading to –1 as the second digit. All the atoms appear as (3,–3) critical points in this analysis as the electron density is maximum at the atoms in all 3 directions.

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The task group met in Pisa, Italy in September 2005 following a discussion meeting in which 12 of the members and 10 outside experts gave presentations. This meeting was followed by E-mail discussions about the definition of a hydrogen bond. The core group (E. Arunan, S. Scheiner (by web-camera), G. R. Desiraju, R. A. Klein, and J. Sadlej) met in Bangalore in September 2006 following which the draft recommendation was produced. Comments from the task group and outside experts helped in refining the write-up. Names of other experts who gave valuable comments are included in the acknowledgments to the technical report [1]. All of the correspondence and presentations are available at the web site: <http://ipc.iisc.ernet.in/~arunan/iupac/>.

REFERENCE

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