

DEFINITION OF THE HYDROGEN BOND

Recommendation submitted by the IUPAC task group (2004-026-2-100)

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* Arunan was the Chairman of the task group and the corresponding author (arunan@ipc.iisc.ernet.in) Scheiner was the co-chairman. Desiraju, Klein and Sadlej were members of the core group that drafted the initial recommendation. Look at following website for more details: <http://ipc.iisc.ernet.in/~arunan/iupac>.

#Other members of the task group listed alphabetically.

39 **1. PREAMBLE**

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41 The task group recommends the definition given here for the hydrogen bond. The
42 short definition is followed by a list of experimental and/or theoretical criteria, which can
43 be used as evidence for the presence of the hydrogen bond. Finally, some characteristics
44 that are typical of hydrogen bonded systems are given. A brief explanation of the terms
45 used is provided after the definition. Moreover, several footnotes (indicated by F#) have
46 been added and these are given at the end. These footnotes are intended to give more
47 explanation for the sake of clarity and completeness. The task group has also produced a
48 comprehensive technical report, which appears elsewhere in this issue of Pure and
49 Applied Chemistry.¹ This report provides a summary of the past work on hydrogen
50 bonding and also the rationale for the proposed definition.

51

52 **2. DEFINITION**

53

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

58

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

66

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

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73 **2. 1. List of criteria**

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75 For a hydrogen bond X–H•••Y–Z:

76

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

81

82 (E2) The atoms X and H are covalently bonded to one another and the X–H bond is
83 polarized, the H•••Y bond strength increasing with the increase in
84 electronegativity of X.^{F3}

85

86 (E3) The X–H•••Y angle is usually linear (180°) and the closer the angle is to 180°, the
87 stronger is the hydrogen bond^{F4} and the shorter is the H•••Y distance.^{F5}

88

89 (E4) The length of the X–H bond usually increases on hydrogen bond formation
90 leading to a red shift in the infrared X–H stretching frequency and an increase in
91 the infrared absorption cross section for the X–H stretching vibration. The greater
92 the lengthening of the X–H bond in X–H•••Y, the stronger is the H•••Y bond.
93 Simultaneously, new vibrational modes associated with the formation of the
94 H•••Y bond are generated.^{F6}

95

96 (E5) The X–H•••Y–Z hydrogen bond leads to characteristic NMR signatures that
97 typically include pronounced proton deshielding for H in X–H, through hydrogen
98 bond spin-spin couplings between X and Y, and nuclear Overhauser
99 enhancements.

100

101 (E6) The Gibbs energy of formation for the hydrogen bond should be greater than the
102 thermal energy of the system for the hydrogen bond to be detected
103 experimentally.^{F7}

104

105 **2.2. Some characteristics of hydrogen bonds**

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

109

110 (C2) Hydrogen bonds are involved in proton transfer reactions (X–H•••Y \rightarrow X•••H–Y)
111 and may be considered the partially activated precursors to such reactions.

112

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

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116 (C4) Hydrogen bonds show directional preferences and influence packing modes in
117 crystal structures.^{F8}

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

122

123 (C6) Analysis of the electron density topology of hydrogen bonded systems usually
124 shows a bond path connecting H and Y and a (3,–1) bond critical point between H
125 and Y.^{F9}

126

127 2. 3. Footnotes

128

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

137

138 F2. Attractive interactions arise from electrostatic forces between permanent
139 multipoles, inductive forces between permanent and induced multipoles, and London
140 dispersion forces. If an interaction is primarily due to dispersion forces, then it would not
141 be characterized as a hydrogen bond. Thus neither $\text{Ar}\cdots\text{CH}_4$ nor $\text{CH}_4\cdots\text{CH}_4$ are
142 hydrogen bonded systems. The importance of various components of hydrogen bonding
143 may vary quite widely from system to system.

144

145 F3. It should be remembered that the electronegativity of the elements could change
146 depending on the chemical environment. This is particularly true of organometallic and
147 other highly polarizable systems. However, it is recommended that no system in which X
148 is less electronegative than H be considered as hydrogen bonded.

149

150 F4. The $\text{X-H}\cdots\text{Y}$ hydrogen bond angle tends toward 180° and should preferably be
151 above 110° . For example, the hydrogen fluoride dimer is nearly linear and is a hydrogen
152 bonded system. However, the lithium fluoride dimer has both LiF molecules oriented
153 anti-parallel because of strong dipole-dipole interactions and would not be considered as
154 being (analogously) lithium bonded.

155

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

162

163 F6. In general, for the donor, the X-H bond length increases and there is an associated
164 red shift in the X-H stretching frequency. There are, however, certain hydrogen bonds in
165 which the X-H bond length decreases and a blue shift in the X-H stretching frequency is
166 observed. It is conceivable that a hydrogen bond could exist without a red or a blue shift.
167 To a lesser extent, in the acceptor, the Y-Z bond deviates from the length of the Y-Z

168 bond in the isolated subunit. The Y–Z bond vibrational frequencies and spectral band
169 intensities also show corresponding changes on hydrogen bond formation.

170

171 F7. For hydrogen bonding to have any practical significance, it should be thermally
172 stable. Hence, a hydrogen bonded complex, between donor and acceptor molecules,
173 produced in a supersonic beam or a cryogenic matrix, may not be found in a room
174 temperature mixture of the two molecules. Moreover, the thermal energy along
175 vibrational coordinates that can destroy the orientational preference should be less than
176 the barrier along those coordinates. This explains why H₂S has 12 neighbours and is not
177 hydrogen bonded when it freezes at – 60° C but shows features of hydrogen bonding at
178 much lower temperatures.

179

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

187

188 F9. Critical points in electron density topology refer to the points where the electron
189 density is an extremum i.e. a minimum or a maximum. The first derivative of electron
190 density is zero in these points and the second derivative would be positive for a minimum
191 and negative for a maximum. A (3,-1) critical point implies that the electron density is an
192 extremum in all three directions leading to the first digit in parenthesis, 3. The second
193 digit is obtained by adding 1 for directions in which the electron density is minimum and
194 –1 for directions in which the electron density is maximum. A (3,-1) critical point is
195 usually found between two atoms that are bonded i.e. along the bond between the two
196 atoms the electron density is a minimum at this point and in the two directions away from
197 the bond, it is maximum thus leading to -1 as the second digit. All the atoms appear as
198 (3,-3) critical points in this analysis as the electron density is maximum at the atoms in all

199 3 directions.

200 **REFERENCE**

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