What is a weak hydrogen bond?

Gautam R. Desiraju
School of Chemistry
University of Hyderabad
Hyderabad 500 046, India
gautam_desiraju@yahoo.com
http://202.41.85.161/~grd/
What is a hydrogen bond?

Under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms instead of only one, so that it may be considered to be acting as a bond between them (Pauling, 1939).

\[ \text{D—H \ldots \ldots \ldots A} \]
Other hydrogen bond definitions, X–H…A

A hydrogen bond is said to exist when (1) there is evidence of a bond, and (2) there is evidence that this bond sterically involves a hydrogen atom already bonded to another atom.

Pimentel and McClellan (1960)

Any cohesive interaction where H carries a positive charge and A a negative charge (partial or full) and the charge on H is more positive than on X

Steiner and Saenger (1993)
Eccentricities of nomenclature

D—H ........ A

H accepts electrons
H donates a hydrogen bond

A donates electrons
A accepts a hydrogen bond

DONOR

ACCEPTOR
Weak (or non-conventional) hydrogen bonds

1937. Glasstone. Cl₃C–H…O=CMe₂ complex

1939. Pauling definition


1967. Oki and Iwamura. O–H…π interactions (JACS)

1968. Donohue criticism of Sutor

1976. Leiserowitz review on carboxylic acids (Acta Cryst)

1982. Taylor–Kennard paper (JACS)
The weak hydrogen bond is an interaction X–H···A wherein a hydrogen atom forms a bond between two structural moieties X and A, of which one or even both are of moderate to low electronegativity (1999).
Bibliography

Different types of hydrogen bond

\[ \text{D—H} \cdots \cdots \cdots \text{A} \quad \text{Very strong} \]

\[ \text{D—H} \cdots \cdots \text{A} \quad \text{Strong} \]

\[ \text{D—H} \cdots \cdots \cdots \text{A} \quad \text{Weak} \]
Hydrogen bond

Any cohesive interaction $X-H\cdots A$ where $H$ carries a positive and $A$ a negative (partial or full) charge and the charge on $X$ is more negative than on $H$

$O-H\cdots O(-)$  $O-H\cdots O$  $N-H\cdots O$

$O-H\cdots \pi$  $N-H\cdots \pi$  $C-H\cdots O$

$Os-H\cdots O$  $C-H\cdots Ni$  $C-H\cdots \pi$
How to assess hydrogen bonds?

- Energy
- Spectroscopy
- Geometry
- Structure
- Function

A complex interaction
<table>
<thead>
<tr>
<th></th>
<th>Very strong</th>
<th>Strong</th>
<th>Weak</th>
</tr>
</thead>
<tbody>
<tr>
<td>[F–H…F]⁻</td>
<td>N–H…O=C</td>
<td>C–H…O</td>
<td></td>
</tr>
<tr>
<td>Energy (kcal/mol)</td>
<td>–15 to –40</td>
<td>– 4 to – 15</td>
<td>&lt; – 4</td>
</tr>
<tr>
<td>IR, νₛ</td>
<td>&gt;25%</td>
<td>5-25%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>Δ(X–H), Å</td>
<td>0.05 to 0.2</td>
<td>0.01 to 0.05</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>H…A, Å</td>
<td>1.2 to 1.5</td>
<td>1.5 to 2.2</td>
<td>2.0 to 3.0</td>
</tr>
<tr>
<td>Shorter than van der Waals</td>
<td>100%</td>
<td>~100%</td>
<td>30-80%</td>
</tr>
<tr>
<td>Effect on crystal packing</td>
<td>Pronounced</td>
<td>Distinctive</td>
<td>Variable</td>
</tr>
</tbody>
</table>
Strong and Weak Hydrogen Bonds, $X\cdots H\cdots O$

An important difference

$O\cdots H\cdots O$

$C\cdots H\cdots O$

$X\cdots O$ distance ($D$) Å
Cl$_{3-n}$R$_n$C–H…O

C–H⋯O Hydrogen Bonds

CHCl₃ and CH₂Cl₂

$d = 1.96\text{Å}
\theta = 162.4°$

$d = 2.88\text{Å}
\theta = 125.3°$
Angles, X–H…O

(a) O–H–O (θ)
(b) C–H–O (θ)
IR bathochromic shifts, C–H…O

Cooperativity

\[ \text{O-H} \cdots \text{O-H} \cdots \text{O-H} \]

\[ \text{R} \quad \text{R} \quad \text{R} \]

\[ \text{Anti-cooperative} \]

\[ \text{O-H} - \text{O} - \text{H} \quad \text{H-O} \]

\[ \text{R} \quad \text{R} \]
C–H…O cooperativity in ethynyladamantan-2-ol

\[ r_1 - r_2 = 0.025(14) \text{ Å} \]

Fig. 2.24. Correlation of the $U$-ratio defined as $U_{\text{eq}}(C2)/U_{\text{eq}}(C1)$ with the distance $d$ in 51 $C\equiv C - H\cdots X$ hydrogen bonds ($X = O, N, \pi$). The horizontal line shows the mean value for $C\equiv C - H$ groups that donate no hydrogen bond with $d < 2.8 \text{ Å}$ (adapted from Steiner 1994b).
Isostructurality

```
\begin{align*}
\text{Et} & \quad \text{Et} \\
\text{O} & \quad \text{Et} \\
\text{N} & \quad \text{Et} \\
\text{H} & \quad \text{Et} \\
\text{O} & \quad \text{Et} \\
\text{H} & \quad \text{Et} \\
\end{align*}
```

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\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{N} \\
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{N} \\
\end{align*}
```

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\begin{align*}
\text{Et} & \quad \text{Et} \\
\text{O} & \quad \text{Et} \\
\text{N} & \quad \text{Et} \\
\text{H} & \quad \text{Et} \\
\text{O} & \quad \text{Et} \\
\text{H} & \quad \text{Et} \\
\end{align*}
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\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{N} \\
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{N} \\
\end{align*}
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Two molecules in the asymmetric unit ($Z' = 2$)
Electronegativity and Hardness

Fluorine

C—H ——— F—C

Weak donor  Very weak acceptor
C–H⋯F–C Interactions in Fluorobenzenes

Thalladi, Weiß et al, JACS, 120, 8702, 1998
C–H···F–C Hydrogen Bonds

All C, H, F compounds

Fluorobenzenes
Weak and reversible C–H···F–C Hydrogen Bridge
Applications. Polymerization catalyst.

Stereoselective polymerisation
Chan et al,
Angew. Chem. Int. Ed.,
42, 1628, 2003

Decrease of β-H transfer
T. Fujita et al,
JACS, 124, 3327, 2002
JACS, 125, 4293, 2003

Boron adducts
Lancaster et al, Chem. Comm.,
2148, 2003

Binding in thrombin
Diederich et al,
Angew. Chem. Int. Ed.,
42, 2507, 2003
Hydrogen bridge *(Wasserstoffbrücke)*

- Electrostatics
- Charge transfer (covalency)
- Dispersion/repulsion (van der Waals)
- Polarisation

A composite interaction
Electrostatic limit (15 kcal/mol)

Covalent limit (40 kcal/mol)

van der Waals limit (0.25 kcal/mol)

very strong hydrogen bonds

strong hydrogen bonds

weak hydrogen bonds

very weak interactions

X=H=H

[HF]⁻
Hydrogen bond

D—H \ldots A

A composite interaction that spans wide ranges of geometry and energy

Great chemical variations among the donor D—H and acceptor A groups

However, all hydrogen bonds have several features in common

Notably, their effect on crystal structure and packing
• Students
• Post-doctorals
• Collaborators
• University of Hyderabad
• DST, CSIR, DRDO