Teaching Tutorial

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Hydrogen bond

Definition, examples, special cases

Course of

General and Inorganic Chemistry

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1. Definition and general features

The typical definition of *hydrogen bond* (or H-bond) invokes the presence of 3 atoms, generally named as X, H and A. X and A can be different elements, whereas H is always hydrogen. Following this convention, we represent the hydrogen bond with a dotted line, as follows:

X-H···A

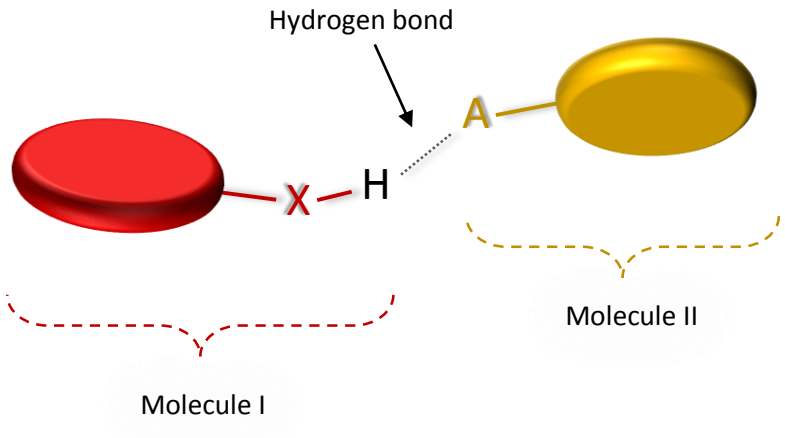
Once we have this model, some requirements have to be fulfilled in order to have a hydrogen bond:

- The dash between the X atom and the hydrogen represents a chemical bond. Thus, its distance is always shorter than the dotted hydrogen bond. If it is not the case, the assignment of the letters and the choice of the line type is wrong.
- **X** has to be a **non-hydrogen atom** and therefore has a higher electronegativity with respect to the bonded H. This results in a polarisation of the X-H bond and a consequent partial positive charge on the hydrogen. **A is generally an electron rich site, usually an element with one or more lone electron pairs**, which therefore attracts the hydrogen because of its localised negative charge.
- There are two useful criteria to evaluate the presence and the strength of a H-bond. The first is to look at the distance between the H and the A atom, which should be shorter than the sum of their Van der Waals radii. A second method suggests to evaluate the angle formed by the X-H···A tern, centered on the H atom: the closer this angle is to 180°, the stronger the H-bond is.

N.B.: *An accurate evaluation of the presence of a real bond between the two moieties of a possible H-bond involves energetic measurements concerning the bond at issue. Therefore, the described criteria are simply good clues about the presence and strength of this type of interaction, but they should not be considered as definitive proofs of its presence or absence.*

If we adopt the X-H···A description, we call X-H the "**hydrogen bond donor**", because it is the chemical group which has a hydrogen to donate, and A the "**hydrogen bond acceptor**" for banal reasons.

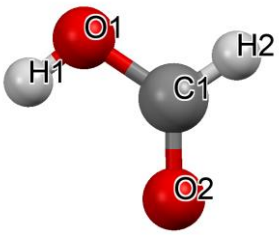
Since often X and A belong to bigger and more complex molecules, we can speak of hydrogen bond between a molecule I and a molecule II, and finally describe the system with the following sketch:



2. Hydrogen bonds in real cases

2.1. General examples

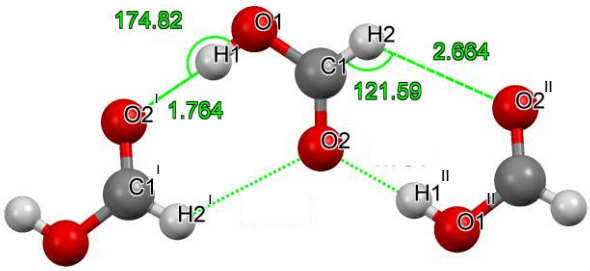
Let us test these concepts by taking a look at a real case. We start considering the crystal structure of formic acid (FORMAC01) and proceed by following **three steps**.



1 – First **we have to identify the atoms which can play the X and the A role** in the hydrogen bond, by simply taking a look at the molecule. X has to be simply bonded to an H, so C1 and O1 can play the X role. Atoms with lone electron pairs are likely to play the A role, in this case O1 and O2. Note that O1 can play both X and A role because it has both the requirements to do that.

So we have two H-bond donors (C1-H2 and O1-H1) and 2 acceptors (O1 and O2).

2 – Now we can **take a look at the real interactions of the molecule with the neighbour ones** in the structure by expanding it in order to **recognise the possible X-H···A terns**. The sequence on the left can be recognised. Therefore, we have:



- X-H···A = O1-H1···O2^{I}
- X-H···A = C1-H2···O2^{II}

All the other possible H bonds in the picture are equal to these two because of the crystal structure symmetry.

3 – Finally, **we evaluate the H···A distance**: if there is a remarkable H-bond, there is a force that keeps the atoms closer than the sum of their Van der Waals radii. In our case we have H and O, whose VdW radii are, according to Pauling's criterion*, 1.2 Å and 1.4 Å respectively. Every X-H···A interaction with H···A shorter than 2.6 Å is therefore a noteworthy hydrogen bond.

In conclusion: the interaction O1-H1···O2^{I} is a strong H-bond, with a bond length of 1.764. On the other hand, the interaction C1-H2···O2^{II} is a very weak H-bond since 2.664 Å is even higher than 2.6 Å. Another confirmation arises evaluating the two X-H···A angles, very close to 180° in the first case (174.82°), very far in the second (121.59°).

Now we can apply the described procedure to evaluate the presence and the strength of H-bonds in any crystal structure. Try on you own taking a look to the following cases:

ETDAMS

NAPHTA04

UREAXX

HIBFON

FOQBAO

SOCLIF

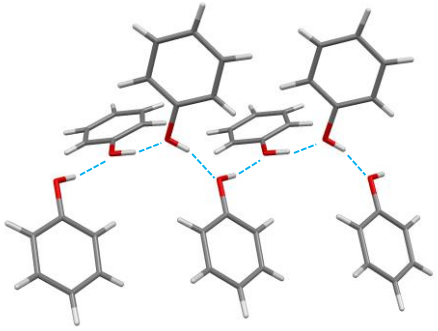
ABEGIY

* Pauling, L., The Nature of the Chemical Bond, Ithaca: Cornell Univ., 1960, 3rd ed

2.2. Special case I: A=X

It's not uncommon that A can be both hydrogen bond donor and acceptor at the same time (in which case the same atom plays the role of A and X). Effectively, if on a X atom one or more lone electron pairs are present, they can attract by means of electrostatic forces an external H atom linked to another X which we can call "X^{I}". By expanding this concept, we can think of hydrogen bond chains connecting different molecules together in a " X-H-X^{I}-H-X^{II}-…-H-X^{n} " fashion.

We can find a similar situation in the crystal structure of phenol (PHENOL03), shown aside in "capped sticks". Can you tell if it happens also in the following cases?



XIBTUY

ABEKUN

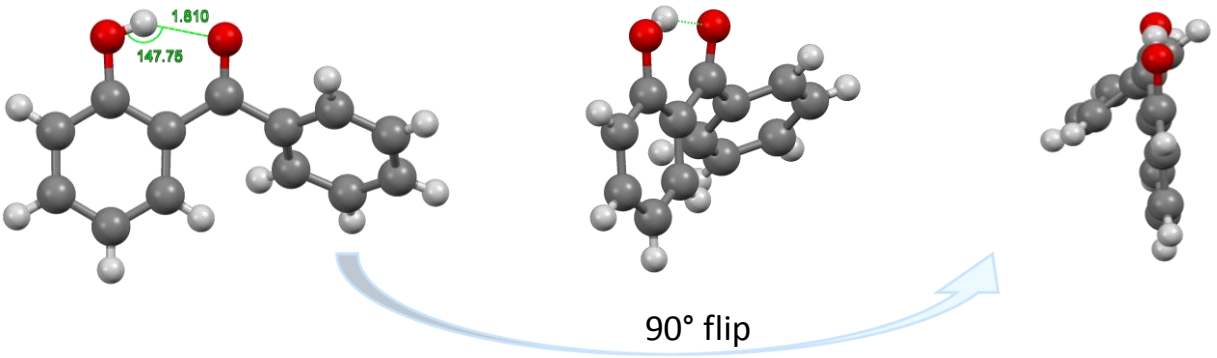
NIYQUH

DEMTEU

FIGYID

2.3. Special case II: Intramolecular hydrogen bond

Sometimes, a hydrogen bond can occur also within the same molecule if its structure allows it. Hence, we can refer to those cases as "**intramolecular** hydrogen bonds", and to the other ones as "**intermolecular** hydrogen bonds". For instance, we can take a look at the molecule in the structure with refcode KEFRAP.



The bond distance is in agreement with the given criteria for a good H-bond, although the angle is far from 180° because of the molecule geometric features. It is worth to note that the O-H bond could in principle point in any direction, but it chooses to stay aligned with the second oxygen to shorten the interaction distance.

Is it always clear whether an intramolecular H-bond is present or not? Try to examine the following cases:

FRUCTO11

GUANPH

INDIGO03

FUJCUI

ABALEV