Versatile Hydrogen

Hydrogen Bond with a Difference

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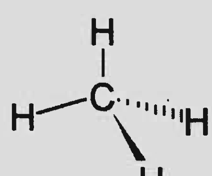
Hydrogen is probably the most intriguing element in the periodic table. Although it is only the seventh most abundant element on earth, it is *the* most abundant element in the universe. It combines with almost all the elements of the periodic table, except for a few transition elements, to form binary compounds of the type $E_n H_m$. Some of these compounds have fascinating structures (**1, 2, 3**).

However the most interesting interaction of hydrogen is the *hydrogen bond.* When a hydrogen atom is bound to an electronegative element it acquires a slight positive charge. As a result, it is attracted to other atoms such as nitrogen or oxygen in the vicinity, which have a slight negative charge. Therefore hydrogen bonds usually have the form X–H···Y in which X and Y are both electronegative atoms. A few examples of hydrogen bonds and their interaction energies are shown in *Table 1.* Although the strength of this interaction is relatively small in most cases, the presence or absence of hydrogen bonds has significant effects on the properties of molecules. Many interesting structural forms resulting from hydrogen bonds were discussed in the article by S Ranganathan (***Resonance***, Vol.1, 4, 1996).

Very recently a new type of hydrogen bond has been experimentally characterised. In most metal hydrides, the hydrogen atom attached to the metal has a slight negative charge. It can be attracted to a hydrogen atom attached to nitrogen or oxygen. Hydrogen bond is formally formed in the unit X–H···H. A hydrogen attached to a metal acts as a hydrogen atom acceptor!



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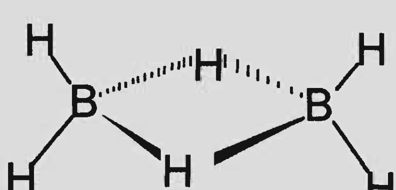

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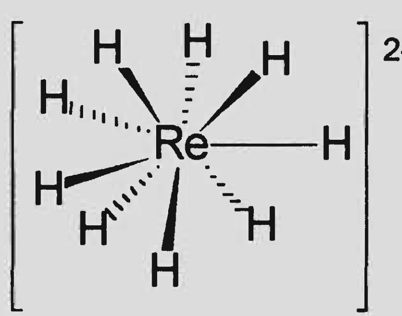

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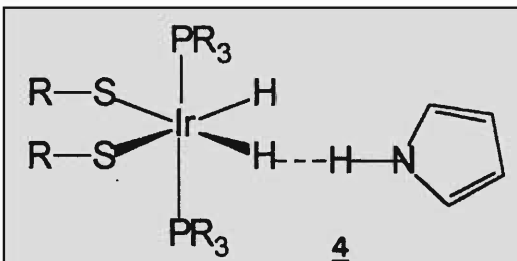
Table 1. Hydrogen Bonds and their strengths

H-Bond	Strength of the interaction in kJ mol^{-1}
$H_2S \cdots H\text{-}SH$	7
$H3N \cdots H\text{-}NH_2$	17
$H_2O \cdots H\text{-}OH$	22
$F\text{-}H \cdots F\text{-}H$	29

Over the last two years, several examples of such interactions have been documented. A typical case is the iridium hydride complex (**4**), hydrogen bonded to pyrrole.

An extremely simple and efficient method to estimate the strengths of this interaction has been evolved by Crabtree and Peris (E. Peris and R H Crabtree, *J C S Chem. Commun.*, 1995, 2179). They measured the energy associated with the stretching of the X–H bond using vibrational spectroscopy. When X–H interacts with an H-M unit, the X–H bond is weakened. The X–H stretching frequency is reduced. The position and also the width of this X–H vibrational band changes. By measuring the vibrational spectra for X–H in the presence and absence of M–H, it is possible to get reliable estimates of the strength of this X–H···H–M interaction. It is found to be a fairly weak bond with a strength of about 4-8 kJ/mol.



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Metal hydrides and hydrogen bond donor molecules have been known for a long time. It is therefore surprising that the interaction between metal hydrides and X–H molecules has been established only recently. However, a plausible reason for this delay may be traced to a reaction of alkali metal and 1st row transition metal hydrides with H–X, where X is very electronegative. Since molecules containing X–H bonds are weak acids they react with the metal hydrides to give molecular hydrogen and M–X rather readily. In other words, the strength of the H···H interaction is so large that it ends up as H_2!

$$M\text{–}H + H\text{–}X \rightarrow M\text{–}X + H_2$$

So what is different in the recently discovered hydrogen bond? In these cases, the metal is from the 3rd or 4th row of the periodic table. The M–H bond is not too ionic and is sufficiently strong. So it engages in weak hydrogen bond

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interactions without reacting to form H_2.

The same type of hydrogen bond has also been proposed for structures involving boron hydrides. The hydrogen atom of the B–H bond has an attractive interaction with hydrogen atoms attached to nitrogen or fluorine. For want of a better name, such X–H···H bonds have been recently christened *dihydrogen bonds*.

Although at first it appears to be a new type of hydrogen bond, the principles involved in its formation are the same as in the classical hydrogen bond. The electronegative element Y carrying a partial negative charge in the usual H–bond has been replaced by a hydrogen that now carries the negative charge through its connection to an electropositive metal. What is truly remarkable is the versatility of hydrogen in combining with electropositive and electronegative elements with equal ease, a fact that has often suggested a special place for it in the periodic table.

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