Hydrogen Bonds

The H bond arises between a weak acid (the donor) and a base (the acceptor). The association between donor and acceptor are related to bond lengths and angles. H-bonds align atoms and hold them at precise distances and angles (important in catalysis as you have seen and will continue to see in your problem sets). The distance between donor and acceptor is always less than it would be if the hydrogen on the donor and the atom acceptor were in simple van der waals contact. The shortened distance between donor and acceptor reflects the bond strength. The H bond that accounts for the majority of macromolecular interactions is between sp^2 lone pair on an acyl oxygen as an acceptor and the nitrogen-hydrogen bond as a donor. There has been some disagreement over the ability of the sulfur to participate as an acceptor in a H bond because of the of overlap between its atomic orbitals and those of nitrogen and oxygen. The existence of such H bonds is supported by the observation that the nitrogen-sulfur distances (3.3 to 3.5 Å) are shorter than the distance expected for van der Waals contacts.

Short strong H bonds (low barrier H bonds) occur when the distance between the heteroatoms is less than the sum of the van der waals radii (effective radius for closest molecular packing).

Atom :van der Waals radius H:1.1Å; O: 1.4; N:1.5; F: 1.35; S: 1.8

An example of a strong H bond in the gas phase is F---H-F where the F---F distance is 2.26 Å and the bond strength is 37 kcal/mole

Table 5–1: Length of Hydrogen Bonds[a]

A–H···B	compounds	average bond length[b] (nm)
OH⊙O	carboxylic acids	0.26 ± 0.01[c]
OH⊙O	phenols	0.27 ± 0.01[c]
OH⊙O	alcohols	0.27 ± 0.01[c]
OH⊙N	all O–H	0.28 ± 0.01[c]
NH⊙O	ammoniums	0.29 ± 0.01[c]
NH⊙O	amides	0.29 ± 0.01[c]
NH⊙O	amines	0.30 ± 0.01[c]
NH⊙N	all N–H	0.31 ± 0.01[c]

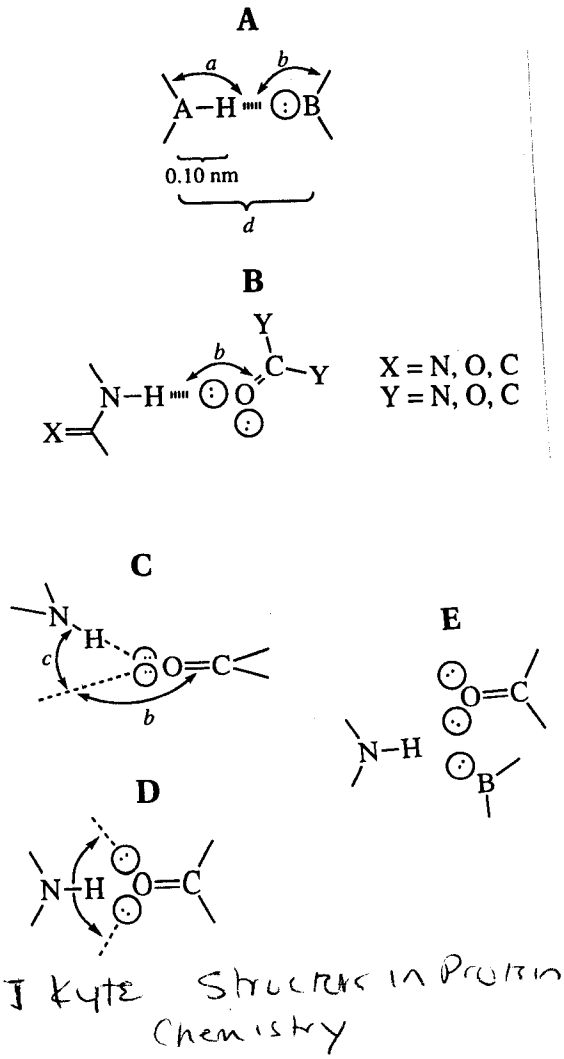

Figure 5–11: Relationships defining bond angles for hydrogen bonds. (A) In a simple hydrogen bond between AH and ⊙B, the line of center between A and B creates an axis, the axis of the hydrogen bond. The angle *a* is the angle between that axis and a σ covalent bond to the atom A. The angle *b* is the angle between that axis and a σ covalent bond to the atom B. The distance *d* is the length of the hydrogen bond. (B) The bond angle *b* for a hydrogen bond between an amido nitrogen and a carbonyl oxygen or an acyl oxygen is the angle between the projection of the axis of the hydrogen bond on the plane defined by the carbonyl group or the acyl group and the σ bond connecting the carbon to the oxygen. (C) The bond angle *c* for a hydrogen bond between an amido nitrogen and a carbonyl oxygen or acyl oxygen is the angle between the axis of the hydrogen bond and the plane defined by the carbonyl group or the acyl group. (D) The bond angle *b* between the axis of a hydrogen bond between a nitrogen–hydrogen donor and the σ covalent bond of a carbonyl oxygen and acyl oxygen can vary over a range bounded by the lone pairs of electrons on the oxygen if the oxygen is otherwise unoccupied. (E) In several instances, the axis of the σ bond between the central atom of the donor and the hydrogen lies between two lone pairs of electrons from two different atoms and one donor interacts with two acceptors.

J Kyte Structure in Protein Chemistry