it is best to have experimental information to use before making that proposal. In the absence of experimental data, or explicit guidance, the default assumption is for one hydrogen bond between any given donor-acceptor pairing.

Predictable hydrogen bonds involving uncharged atoms. Based on experiment, there are a few generalizations about predicting when a hydrogen bond will be possible.

Forming significant hydrogen bond donors is predictable when hydrogen atoms are covalently bonded to nitrogen, oxygen, or fluorine atoms (N-H, O-H, F-H). And comparably, the nonbonding electron pairs on nitrogen, oxygen, or fluorine atoms can serve predictably as hydrogen bond acceptors (N:, O:, F:). Other bonds involving hydrogen atoms can be donors, and other atoms can be acceptors, but not as predictably, so experimental evidence is needed.

Atom size appears to make a difference. Even though chlorine has the same electronegativity as nitrogen, uncharged chlorine atoms are not significantly involved in hydrogen bonding. Chlorine, in the third period of the periodic table, has larger atoms than those of fluorine, oxygen, or nitrogen (the chlorine atom radius is 1.75 Å, while the fluorine, oxygen, and nitrogen atoms are 1.47, 1.52, and 1.55 Å, respectively). We imagine that the valence electrons on a chlorine atom are more diffuse and are not shared with the small hydrogen atom (radius 1.20 Å) as effectively.

Electronegativity differences play a role, too. Hydrogen atoms bonded to carbon are not predictably involved in the formation of hydrogen bonds because the bond polarity is too low. Again, this does not rule out CH bonds as hydrogen bond donors, but, as stated above, experimental evidence for a phenomenon is all that is needed to support an argument for a counterexample to the N/O/F generalizations.

Figure 0252 summarizes nine pairings of hydrogen bond donors with hydrogen bond acceptors that are formed predictably. The higher electronegativity of fluorine makes the HF bond the most polar, and so the best hydrogen bond donor in this group. The same electronegative property of fluorine means that its atoms are less likely to share their electrons with another atom, and so, for the same reason, it is the poorest hydrogen bond acceptor.

Figure 0252

Hydrogen bonds form predictably when the donors and acceptors involve nitrogen, oxygen, and fluorine atoms.