Understanding hydrogen bonds?

New measurements of simple complexes of hydrogen fluoride and nitrous oxide have thrown light on the properties of two quite distinct kinds of hydrogen bonds.

ALL of us know that hydrogen bonds are important, for example in making the structure of water peculiar, in holding the two strands of DNA together or in accounting for the ways in which protein molecules cohere with themselves, but few of us know what hydrogen bonds are like. That is why we should all be grateful to Christopher M. Lovejoy and David J. Nesbitt of the US National Bureau of Standards at Boulder, Colorado, for another set of infrared (or vibrational and rotational) spectra of unlikely molecular complexes — this time between nitrous oxide (N_2O) and hydrogen fluoride (HF), as reported in the latest issue of *J. Chem. Phys* (**90**, 4671; 1989).

Bonding, very much a chemist's concept, suggests interatomic links that endure for the rest of time. Tie atoms of carbon and hydrogen together and you have an interatomic link that may at one stage be part of a benzene ring and, at another, a constituent of some methane molecule discharged from an oil-well in the Persian Gulf. Bonds like that, of course, are distinguished by the energy required to break them, essentially of the order of one electron volt (1 eV), which is equivalent to a Boltzmann temperature of 10,000 K in round numbers. Hydrogen bonds, by contrast, are less durable by a factor of 100, which means that they are breaking and reforming repeatedly at room temperature. But none of that implies that hydrogen bonds are not bonds: it is partly that they are labile, partly that they are in danger of being confused with other kinds of inter-molecular interactions, van der Waals forces for example.

The distinction, admittedly, is not nearly as sharp as one might wish. Take, for example, a mixture of argon and hydrogen chloride (Ar and HCl). Pure argon is a near-perfect perfect gas, but even quite small proportions of HCl will make the gas laws go awry — the virial coefficients that measure departures from Boyle's law (*PV* is a constant) are surprisingly large and often opposite in sign from what might be expected. Happenings like that should have pointed to the likelihood that atoms of the inert gases can form compounds long before they were discovered.

The natural link between HCl and Ar atoms is that in which the H is situated geometrically between the two heavier atoms, the Ar and the Cl. There, as a simple proton, it can alternatively rob either the rare gas atom or the chlorine ion of an electron (reverting to atomic status itself). That is how Pauling would have put it in the first edition of *The Nature of the Chemical Bond*. What the experiments show is something different. Ar-HCl is relatively stable, but there is also evidence that Ar-ClH has a transitory existence. Plainly, what matters most is the polarizability of completed electron shells, with the complication (for those who solve Schrödinger wave equations for a living) that it is not easy to know what to make of the Born–Oppenheimer approximation (which supposes the motions of all nuclei to be slow) when there is a rogue proton to account for.

That is why it seems safer to think of hydrogen bonds as dynamic structures, which is nicely illustrated by the tendency of molecules such as hydrogen fluoride (HF) to form dimer molecules. Why dimers? And, if so, how is it determined which of two HF molecules contributes the intermediate proton to the complex? The predictable answer, of course, is neither. At any reasonable temperature, one or other or both molecules will be rotating. For practical purposes, the F atoms will be the dogs and the H atoms their tails. If interposed protons make for binding in some degree, a viable $(HF)_2$ complex will be a four-atom molecule in which one or other of the hydrogens will be roughly half-way between the two fluorines for much of the time. A little thought, of course, will show that there are two ways in which that may be accomplished — the HF molecules may be spinning in the same or in opposite directions. That means that there are two states for the hydrogen bonded dimer, whose energy differs by a frequency measured in MHz. There was an elegant paper in *J. Chem. Phys.* a few months ago that demonstrated just that.

What Lovejoy and Nesbitt have to say has much in common with that tale, but relates to the dimers formed by hydrogen bonding between HF and N_2O (nitrous oxide) — not the symmetrical molecule that might be imagined, but one that has a nitrogen atom in the middle.

There are two ways in which hydrogen bonds may be formed: the H of HF is adjacent either to the terminal oxygen or to the terminal nitrogen. It turns out that the link with the terminal oxygen is the more stable, but that the resulting five-atom hydrogen molecule is bent. In the language of the elementary chemistry text-books, the terminal oxygen has two 'lone-pairs' of electrons, sticking out sideways from the linear N_2O molecule an an angle not very different from the tetrahedral angle, with each of which an HF molecule may make an advantageous linear connection.

Lovejoy and Nesbitt have found spectroscopic evidence to bear out the existence of the other form in which the H of HF is bonded to the terminal N of N_2O. Their experimental technique is horrendous as, these days, these matters are. Hydrogen-bonded molecules are formed as a supersonic stream from a high-pressure nozzle (which has the virtue of cooling the the molecules almost to absolute zero) and their vibrational spectra recorded with a laser system with a resolution of roughly 6 MHz. The familiar problem of the analysis is to fit the lines in the rotational and vibrational spectrum of the possible molecules to those actually observed. Among the complications of the analysis are the need to take account of the distortions of both kinds of molecules under the influence of centrifugal forces, which stretch the linear complexes and straighten those in bent form.

The bearing of all this on hydrogen bonds in general is not as remote as it might seem. The benefits of a spectral analysis of the kind described by Lovejoy and Nesbitt is that it is possible to estimate the force constants of the bending motions in which the directions of the linear and bent hydrogen bonds are displaced from their equilibrium positions. What that analysis shows is that, while the linear hydrogen bond (FH-NNO) is the more stable, it is also the more rigid. All that is explicable in terms of simple arm-waving about the directionality of different kinds of hybridization between *s* and *p* orbitals.

All of this is, of course, a long way from the proper understanding of how strands of DNA are held together, let alone from an understanding of the structure of liquid water. But it is a lot better than nothing that it now seems possible to measure the mechanical properties of the most shadowy, if also the most important, of all chemical bonds. Nobody would suggest that the time has come to start calculating with hydrogen bonds as if they were familiar aliphatic CH bonds, but the time when that is possible may not be far off.

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