HYDROGEN BONDING IN THE METHANOL DIMER

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Abstract

In this work, two methanol molecules are placed in different arrangements to study hydrogen bonding in carbohydrate materials such as cellulose. Energy was calculated as a function of both hydrogen bond length and angle over wide ranges, using quantum mechanics (QM). The QM wavefunctions are analyzed in terms of R. F. W. Bader's “atoms-in-molecules” theory. “Bond critical points” and “bond paths,” indicators of bond formation, were found over H...O distances from 1.5 to 3.5 Å, and O-H…O angles greater than 110°. Therefore, a wide range of geometries, especially those with long H…O distances, can correspond to hydrogen bonds. This range is wider than allowed by some geometric criteria.

Introduction

When examining a proposed crystal structure or computer model of cellulose, it is often desirable to know what forces stabilize that particular arrangement. Hydrogen bonding is almost universally acknowledged to be a major force in solid-phase cellulose (Krässig, 1993). There are intra- and intermolecular hydrogen bonds, and the latter can be within a crystal, between crystals in a fiber, or even between fibers in a structure such as paper. Although we are accustomed to viewing drawings or physical models of molecules, they are just cartoons to aid our understanding of the locations of the atoms and the connectivity between the atoms. For carbohydrate molecules, the covalent bonding between atoms is sufficiently well understood for us (our software) to confidently draw a bond or “stick” between two balls that represent atoms. Because the forces in hydrogen bonds are weaker by an order of magnitude or more, however, our confidence in assigning hydrogen bonds is considerably less. In many cases, the atoms are in positions that could correspond to a hydrogen bond, but do not correspond to an ideal geometry. How can it be known that a hydrogen bond really exists? In particular, one of the proposed hydrogen bonds in native cellulose has an H…O distance of 2.72 Å (Nishiyama et al., 2008), and the present work resolves a question about its legitimacy.

Criteria have been developed within several paradigms for ascertaining whether a hydrogen bond exists. For classic O-H...O interactions, the simplest criterion might be based on the distance between the two oxygen atoms. If they are closer together than some distance that corresponds to twice their van der Waals radius (2 × 1.52 = 3.04 Å), then they could be hydrogen bonded. That simple criterion can be used for X-ray studies of fibers when the location of the hydrogen atom is unknown. More elaborate criteria are used in the PLATON program (Spek, 2003) for analyzing crystal structures. The program decides that a hydrogen bond exists if the following tests are satisfied, where (see Figure 1) d is a distance, D is the donor, A is the acceptor and R is the van der Waals radius.

d(D...A) < R(D)+R(A)+0.50:	d(O...O) < 1.52 + 1.52 +0.50 = 3.54 Å
and if d(H...A) < R(H)+R(A)-0.12:	d(H...O) < 1.20 + 1.52 – 0.12 = 2.60 Å
and if Ang., D-H...A > 100.0°:	the O-H...O angle > 100°

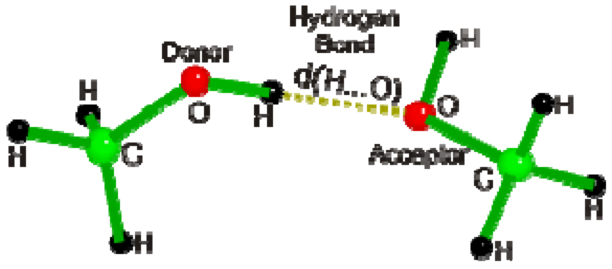

Figure 1. The hydrogen-bonded methanol dimer, with the donor molecule on the left and the acceptor molecule on the right.

Other criteria based on atom positions are more complex. In the world of proton NMR, evidence of effects of hydrogen bonding on chemical shifts has been available for nearly 60 years. In the case of quantum mechanics modeling studies, two approaches are currently fashionable, following the early work (Umeyama and Morokuma, 1977) on deconvoluting the wavefunction to yield the various contributions. One modern approach, the Natural Bond Order method (Reed et al., 1988), depends on examination of the different bonding and antibonding orbitals for evidence of charge transfer. The other relies on Richard Bader's atoms in molecules (AIM) theory (Bader, 1994). That method, which we employed for the present project, analyzes the electron density from either a quantum mechanics study or from a high-accuracy X-ray diffraction crystal structure. AIM theory is used extensively for study of hydrogen bonding (Grabowski, 2006). A distinguishing feature of our work is that we have studied a wide, systematically incremented range of hydrogen bond geometries that are not at equilibrium. This range covers the geometries that might be encountered in various crystal structures of carbohydrates, including cellulose.

Materials and Methods

Koch and Popelier (1995) described the electron density gradient analysis (or AIM) criteria for C-H...O hydrogen bonds. This is of special interest because C-H...O hydrogen bonds are also thought to have a role in molecules related to cellulose, and probably in cellulose as well. Their criteria are also directly applicable to O-H...O hydrogen bonds. In all, Koch and Popelier described eight characteristics of hydrogen bonds, but the two major ones are the existence of a bond path and a bond critical point (BCP). If these are present, then a bond is said to exist. A BCP is one of the locations in the electron density where the gradient of electron density, $\nabla\rho(r)$, is zero, with the other critical points for nuclei, for rings and for cages. A bond path corresponds to the ridge of electron density between two bonded atoms and is identified by the gradient vector of the density between the nuclei, passing through the BCP. These criteria are followed by ranges of values for the electron density at the BCP and a demand that the second derivative of the electron density at the BCP (termed the Laplacian) is positive. Other characteristics of hydrogen bonds include changes in the atomic volumes and charges but a bond path and a BCP suffice for determining whether there is a bond.

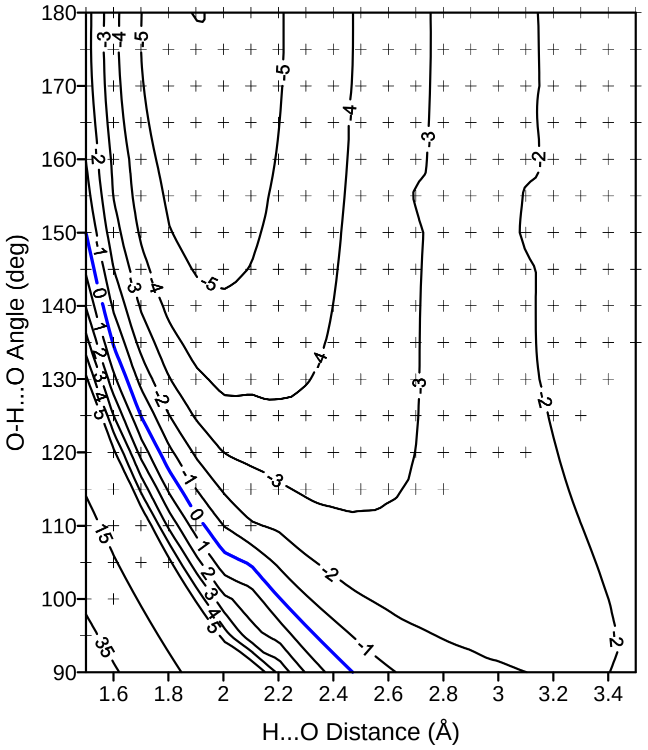

Figure 2. Contours of potential energy are shown for the varied hydrogen bond distances and angles. Locations where H…O BCP were found are indicated by + signs. The minimum relative energy, −5.75 kcal/mol, is indicated by the very small contour at the top of the drawing (1.9 Å, 180°). Contours are in kcal/mol; experimental structures

are not expected to occur to the left of the blue line (0 kcal/mol).

Two methanol molecules were arranged in 399 mutual orientations so that the H...O distance varied from 1.5 Å to 3.5 Å and the O-H...O angle ranged from 90° to 180°. At each increment of variation, the energy was minimized with the B3LYP method and the 6-31+G* basis set, using the Gaussian 03 (Frisch et al., 2004) QM software. A final energy was calculated with that geometry using the larger, 6-311+G** basis set. The corresponding wavefunction was processed by the AIMAll program (Keith, 2008) for analyzing electron density. With this fairly large basis set that includes a diffuse function (represented by the + sign), Basis Set Superposition Errors should be less than a kcal/mol (Lii et al., 1999) so no corrections were made. Frequencies were not calculated because of the constraints on hydrogen bond geometries (none of the structures were at minima).

Results and Discussion

We used methanol molecules as stand-ins for cellulose chains that could be hydrogen bonded to each other. These stand-ins have small size, allowing fairly rapid calculations, while still having chemical similarity to the hydroxyl groups of cellulose (i.e., the hydroxyl groups are bonded to sp^3 carbons in methanol and cellulose). Fairly comprehensive studies of the methanol dimer date to Jorgensen (1979), who used STO-3G quantum mechanics calculations on 270 random geometries of the dimer to derive an empirical potential function for modeling interactions with methanol. Those models extended knowledge of hydrogen bonding energies and geometries to molecules that incorporated non-polar groups. Besides the minimal level of quantum mechanics in that early work, another limitation was that in most of the calculations, the geometry was held fixed, with no adjustments within the molecule in response to the formation of hydrogen bonds. These subtle variations, described by Koch and Popelier, were monitored in the present work but will be discussed elsewhere. Also, Jorgensen did not address the question of whether there was actually a bond; AIM theory was just being developed at that time (Bader, 1979).

As shown in Figure 2, the ideal geometry (the one giving the lowest energy) of the methanol dimer had an H...O distance of 1.90 Å and an O-H...O angle of 180°. The energy for the ideal geometry was –5.75 kcal/mol, compared to two methanol molecules at infinite separation. These results are within the expected ranges for such calculations on O-H…O hydrogen bonds (Grabowski, 2006). This is a greater stabilization than might be found with a very large calculation that would not be suited for 399 increments of structure. The energy was very dependent on the H…O distance, less so on the angle. BCP were found for the O-H...O bond in the locations indicated by a plus sign.

Figure 2 shows that BCPs were not found when the O-H…O angle was less than 110° despite the existence of attractive interactions (energy < 0). Further examination of the results from the AIMAll program showed that other attractions occurred to lower the energy in the places where O-H…O BCPs were not found, specifically C-H…O hydrogen bonds. The acceptor methanol molecule had rotated during energy minimization in those cases because the energy could be lowered more by formation of these otherwise weaker hydrogen bonds.

Compared to the criteria from the PLATON program for the existence of hydrogen bonds, the above map suggests that hydrogen bonds can be stabilizing at considerably larger H…O distances than the 2.6 Å value from PLATON. At the 2.6 Å value, the calculated energy is about 3.5 kcal/mol, still quite stabilizing, and H…O distances as long as the maximum PLATON O…O value of 3.54 Å would still provide more than 1 kcal/mol of stabilization. On the other hand, the O-H…O angle may need to be 10° or 15° larger than PLATON's value of 100° for a BCP to occur. The above-questioned hydrogen bond in native cellulose, with H…O = 2.72 Å, O…O = 3.29 Å and O-H…O of 117° meets these AIM criteria and should be accepted as a hydrogen bond. However, it would still be useful to carry out an AIM analysis on the exact structure from that experimental work.

Summary

When analyzing 3-dimensional structures, either from experiment or molecular modeling calculations, it is sometimes difficult to decide whether a particular geometric arrangement corresponds to a hydrogen bond that is contributing to the stability of the structure. We have analyzed 399 different arrangements of the methanol dimer as stand-ins for hydrogen bonds that might occur in cotton cellulose. Quantum mechanical wavefunctions (generated with Gaussian 03) were searched with AIMAll for bond critical points that would indicate whether hydrogen bonds were formed. It is fair to say that a hydrogen bond, with some shared electron density, does exist if there is a bond critical point for the proposed interaction. Bond critical points were found for a wide range of methanol dimer arrangements. The information in Figure 2 could be used to establish new geometric criteria, but it refers only to structures that were optimized while maintaining the specified hydrogen bond length and angle. It is possible that BCPs for O-H…O hydrogen bonds could have been formed if the acceptor molecule were adjusted to another (higher energy) orientation while still meeting the H…O and O-H…O geometry in Figure 2, Also, experimental geometries in complex structures will probably not correspond exactly to these minimized models. This work demonstrates that the hydrogen bonding proposed for different cellulose crystal structures, currently based strictly on geometric criteria, could be profitably re-examined.

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