Acknowledgment. This work was supported by National Science Foundation Grant CHE 75-14460 to J.R.S. and a University of Illinois Fellowship to G.F.S. A loan of iridium trichloride from Engelhard Industries is also acknowledged.

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(13) $Ir_4(CO)_{11}PPh_2Me$ and $Ir_4(CO)_{10}(PPh_2Me)_2$ were prepared as previously reported.[12] $Ir_4(CO)_9(PPh_2Me)_3$ and $Ir_4(CO)_8(PPh_2Me)_4$ were prepared by further reaction with stoichiometric amounts of Me_3NO and PPh_2Me in refluxing benzene. The use of Me_3NO to promote substitution of carbonyl ligands in tetranuclear iridium clusters has proven to be a general reaction. These reactions will be reported separately.

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(17) ^{13}C spectra were obtained using samples enriched with ^{13}CO to a level of 30–50%, as judged by mass spectrometry. Spectra were obtained on a Jeol FX-60 spectrometer operating at 15.03 MHz. Coupling constants were confirmed by recording the spectra on a Varian XL-100 spectrometer operating at 25.15 MHz. $Cr(acac)_3$ (0.03 M) was added as a relaxation agent for the carbonyls.

(18) The ^{13}C NMR spectrum for $Ir_4(CO)_8(AsPh_2Me)_4$ has been reported: 223.7 (1), 220.3 (2), 175.5 (2), 169.1 (1), and 135.6 (2).[11] We feel that the signal at 135.6 ppm is very likely due to the phenyl carbons of the arsenic ligands.

(19) The doublet due to carbonyl g is observed to broaden, shift downfield, and decrease slightly in separation between −88 and 2 °C. We attribute these effects to a small but nonnegligible population of the radial isomer (e.g., **8**), whose relative proportion increases with temperature. (Similar effects have been observed for $H_4Ru_4(CO)_{11}P(OMe)_3$.[20]) We have not established another isomer from the limiting ^1H or ^{31}P NMR spectra (detection limits ca. 5%), but temperature-dependent chemical shifts also suggest exchange with an additional species. $Ir_4(CO)_{11}PPh_3$ shows essentially identical ^{13}C spectra over a similar range of temperatures, except that the doublet from carbonyl g shows much less perturbation with temperature up to the point equivalent to the 2 °C spectrum in Figure 1. Furthermore, separate isomers can be distinguished within the set of $PPhMe_2$ derivatives, indicating that the preference for axial substitution decreases in the order $PPh_3 > PPh_2Me > PPhMe_2$. This and other trends will be discussed in a full paper concerned with the complete set of compounds that we have studied.

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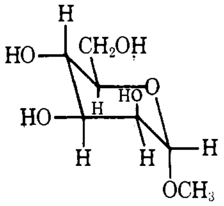
Some Experimental Observations on H···O Hydrogen-Bond Lengths in Carbohydrate Crystal Structures

Sir:

The completion of the neutron diffraction studies of of three crystal structures of carbohydrates with related configuration and conformation has revealed an unusually systematic relationship between the hydrogen-bond lengths and the type of O—H···O interaction. Although hydrogen bonds are the predominant cohesive forces in crystals of polyhydric organic compounds including the carbohydrates, many of which have been studied by x-ray diffraction, simple relationships involving the hydrogen-bond distances are not generally observed. This is because in these *molecular* crystals the hydrogen bonding depends not only upon the stereochemistry of the donor and acceptor groups involved but also upon the way in which the molecules as a whole can pack to form a regular three-dimensional lattice. The structure of a particular hydrogen-bonding scheme is not determined solely by the requirement of maximum hydrogen-bond energy, but rather represents a compromise between this and the optimization of the other intermolecular forces.

The three crystal structures are those of the monosaccharides methyl α-D-mannopyranoside (**1**),[1] methyl α-D-glucopyranoside (**2**),[1] and methyl α-D-altropyranoside (**3**),[2] in which there are representative examples of five different modes of interaction between donor hydroxyl groups and acceptor oxygen atoms.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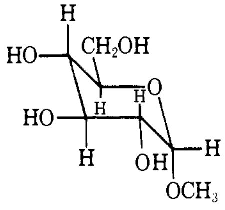
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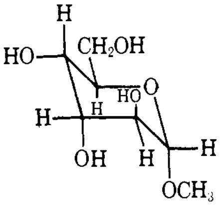
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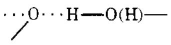
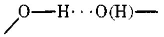
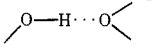
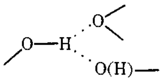
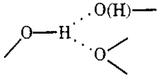
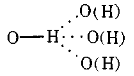
As shown in Table I, each mode has associated with it two or more hydrogen-bond distances which appear to be characteristic within a relatively narrow range. These values fall into five distinct groups which are separated by about 0.1 Å.[3]

The shortest hydrogen bonds are those in which the hydroxyl oxygen is a hydrogen-bond acceptor, as well as functioning as a hydrogen-bond donor. This type of bonding is the most common in carbohydrate crystal structures and is responsible for the very frequent occurrence of chains of hydrogen bonds. This cooperative strengthening of hydrogen bonding has been predicted from theoretical studies of water polymers,[4] and is further discussed in the following communication.[5] In the absence of the acceptor function of the hydroxyl oxygens, the bonding is weaker, as shown by the two examples with significantly longer bond lengths. Hydrogen bonds from hydroxyls to the ring or glycosidic oxygens also occur in many carbohydrate structures but they are noticeably less common than those between two hydroxyls.[6] This is consistent with weaker bonding and the observed increase in the H···O bond distances. Bifurcated hydrogen bonds are even rarer, though the structure of methyl α-D-altropyranoside did provide two examples in which the H···O separations are less than the normal accepted sum of the van der Waals radii, 2.4 Å. Finally, there is an example of a nonbonding environment; however, the fact that the nearest neighbor atoms to the hydrogen are oxygens indicates that there may still be some specific H···O interactions not necessarily directional enough to be described as bonds.

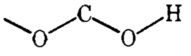
With some exceptions, a similar distribution of hydrogen-bond lengths is found in the crystal structures of α-D-glucose[7] and sucrose,[8] for which the neutron diffraction data are also given in Table I. In the α-D-glucose structure the four donor-acceptor hydrogen-bond lengths have a longer mean value than in the methyl pyranosides by about 0.02 Å, but span a similar range of distances. The hydroxyl-to-ring oxygen hydrogen

Table I. Hydrogen-Bond Lengths in Different Types of Hydroxyl–Oxygen Interactions in Some Carbohydrate Structures[14] Studied by Neutron Diffraction

	H···O distances[a]			
Type of interaction	Methyl pyranosides	α-D-Glucose	Sucrose	β Maltose monohydrate[e]
Hydroxyl–hydroxyl donor/acceptor 	1.736[b] 1.810[c] 1.738[d] 1.770[d] 1.772[d]	1.756 1.757 1.817 1.820	1.760 1.851[g] 1.892 1.907 1.908	1.812[f] 1.824 1.846 1.849 1.927
Hydroxyl–hydroxyl donor only 	1.922[b] 1.917[c]		1.921	1.835[g]
Hydroxyl–oxygen 	1.998[c] 2.052[c]	1.914[f]	1.895[g]	
Bifurcated bonds 	{2.085[b] 2.140 {2.138[b] 2.185			
Nonbonding 	{2.328[d] 2.633[d]		2.309 2.534 2.539	

[a] The standard deviations of these distances are 0.002 to 0.005 Å. They are uncorrected for thermal motion effects which could shorten the H···O bonds by about 0.02 Å, except for the nonbonded hydrogen where the corrections will be greater. [b] Methyl α-D-altropyranoside. [c] Methyl α-D-mannopyranoside. [d] Methyl α-D-glucopyranoside. [e] These data exclude the hydrogen bonds involving the water molecules, which are four-coordinated. [f] Hydrogen bond from an anomeric hydroxyl. [g] Intramolecular hydrogen bond.

bond is 0.1 Å shorter than the corresponding category for the methyl pyranosides and corresponds better with the distances in the O—H···O(H) group. It should be noted, however, that the hydrogen involved in this bond is that of the anomeric hydroxyl, which is the chemically unique labile hydroxyl group responsible for the mutarotation in solution, not present in the methyl pyranosides. Those features of the electronic structure of the hemiacetal group



which are believed to give rise to the *anomeric effect*,[9] might also be expected to lead to enhanced hydrogen-bond strength. This is discussed in more detail in the following paper.[5]

In the sucrose structure, the donor–acceptor hydrogen-bond lengths have a significantly longer mean value, and cover a wider range of distances, although they do not quite extend to those of the next category. This we believe is a consequence of the more complex packing requirements of the larger disaccharide molecule. The hydrogen-bond length which is conspicuously out of place is that to the ring oxygen, being much shorter than those in the methyl pyranosides. This is the intramolecular bond between the glucose and fructose residues. Its length will be strongly influenced by the intramolecular geometry of the two rings and again it has no counterpart in the methyl pyranoside structures. The nonbonding interactions in the sucrose structure agree closely with that in methyl α-D-glucopyranoside, except that three oxygen atoms are involved instead of two.

Neutron diffraction data are also available for the structures of β-maltose monohydrate,[10] D-glucitol,[11] two forms of potassium D-gluconate monohydrate,[12] and L-ascorbic acid.[13] In β-maltose monohydrate the hydrogen bonding includes water molecules, which are involved in four bonds at chain intersections. Excluding these, the H···O bond lengths span a narrower range than in sucrose and the shortest bond is that from the anomeric hydroxyl. Neither the glycosidic linkage nor the ring oxygens are hydrogen bonded. As in sucrose, we believe that the longer hydrogen-bond distance as compared with the monosaccharide data is a consequence of the more complex packing requirements of the disaccharide molecules, combined in this case with the adjustments necessary to include the water molecules in the crystal lattice.

The D-glucitol hydrogen-bond structure[11] is most unusual in that it consists of two infinite chains; one of which has bond lengths shorter than normal (1.691, 1.723, 1.729 Å), while in the other they are longer (1.914, 2.018, 2.128 Å). These differences cannot be related to the O—H···O angles, all of which lie between 163° and 178°. Clearly other packing factors (long-range dipolar and van der Waals forces, and possibly short-range repulsive forces as well) play an important role in determining these hydrogen-bond lengths, compressing them in one direction and expanding them in the other, when compared with similar bonds in Table I. The ascorbic acid and potassium gluconate hydrate structures are further complicated by the presence of acceptor atoms other than hydroxyls and acetal oxygens and the correlations we have described above are neither expected nor observed.

Acknowledgment. Research was performed under the auspices of the U.S. Energy Research and Development Administration and supported by NIH research grant GM-21794.

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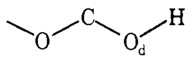
Theoretical Observations on the Structural Consequences of Cooperativity in H···O Hydrogen Bonding

Sir:

Neutron diffraction studies on three methyl pyranosides reported in the preceding communication[1] have uncovered a strong correlation between hydrogen-bonded OH···O distances and the chemical environment of the proton-donor oxygen atoms. That such effects should emerge from crystal data is quite significant since the easily deformable hydrogen bonds are in competition with other crystal packing factors, and one may infer that the data are revealing fundamental aspects of hydrogen bonding worthy of theoretical analysis. In particular, the pyranoside results together with previous neutron data for the related pyranose, α-D-glucose,[2] suggest that an H···O bond-length shortening of ~0.1 Å can be attributed to cooperative effects which occur when the proton donor oxygen (O_d) is also (1) a proton acceptor (-H···O_d—H···) or (2) a hemiacetal oxygen atom



which gives rise to the anomeric or gauche effect.[3] The latter type of cooperativity involves an intramolecular resonance phenomenon (the source of the gauche effect) and is thus somewhat different from the former type, which involves two sequential intermolecular hydrogen bonds. The consequences of cooperativity on hydrogen-bond lengths implied by the neutron data have led us to carry out model ab initio studies which are summarized in the present communication, and which provide an a priori measure of the expected magnitude of the effect as well as a basis for a detailed theoretical understanding.

The cooperative interaction of the proton-donor and proton-acceptor functions in linear-chain hydrogen-bonded polymers has been the subject of many detailed theoretical treatments,[4-7] but major emphasis has been on the analysis of the energetics, with relatively little attention paid to corresponding structural effects. Some studies of linear-chain water[4b] and alcohol[7a] polymers have employed the hydrogen-bonded OH···O distance appropriate to the dimer, and the extent of H···O bond shortening in the water trimer (relative to the dimer) remains uncertain: the minimal basis molecular orbital study of Del Bene and Pople[4a] predicted a large decrease (0.10 Å), whereas the more accurate near-Hartree-Fock results of Hankins, Moskowitz, and Stillinger[5a] suggest little if any change.[8,9] The latter study, however, was primarily concerned with cis dimer conformations peculiar to the ice Ih structure and did not report the actual equilibrium H···O distance for the trimer. Experimental resolution of this question for the case of water is complicated by the occurrence of chain branching in the condensed phase.[10] Alcohols are simpler, however, in that they generally form finite or infinite linear chains, many examples of which are provided by the neutron diffraction data.[1,2,11]

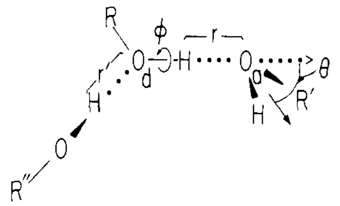


Figure 1. Schematic representation of hydrogen-bonded dimers and trimers, indicating H···O bond lengths (*r*,*r*′), the angle (θ) between the H···O vector and the plane of the proton acceptor $R'O_aH$, and the torsion angle (φ) between the bisector of the proton acceptor bond angle ($R'O_aH$) and the O_dR bond of the proton donor. The plane formed by the bisector of the proton acceptor and the H···O vector is constrained to be perpendicular to the plane of the proton acceptor. The torsion angles are governed by the conventions introduced by Klyne and Prelog.[19] The figure corresponds to φ = 180° and the arrow (↻) shows the sense of rotation of O_d–R associated with *increasing* φ. In the case of trimers, the donor oxygen O_d also serves as an acceptor, and angles θ′ and φ′ are defined analogously to and set equal to θ and φ, respectively.

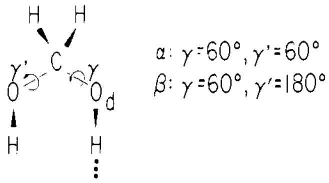


Figure 2. Methanediol as a model for the hemiacetal or anomeric proton-donor oxygen atom (O_d). The conformations designated as α and β are models for α and β pyranose rings, respectively (cf. ref 3). The structure displayed corresponds to the α conformation. The torsion angles γ and γ′ refer to the HOCO sequences and follow the conventions described for Figure 1 (the circular arrows indicate the rotations of the OH bonds which correspond to increasing γ or γ′). The geometrical parameters are based on pertinent carbohydrate structural data[20] (r_{CO_d} = 1.39 Å; r_{CO} = 1.43 Å; ∠OCO_d = 112° (α), 107° (β)) or energy optimization (∠HCH = 110°). The bisectors of ∠HCH and ∠OCO_d coincide and the corresponding planes are perpendicular (by constraint).

Accordingly, detailed theoretical structure comparisons of linear-chain dimers and trimers of alcohols are warranted as well as examination of the other type of cooperativity noted above (i.e., that associated with the gauche effect[3]), which to our knowledge has not received prior attention in the literature. Toward this end we have selected several model systems involving methanol or methanediol (see Figures 1 and 2) as the proton donor and have carried out molecular orbital calculations with an extended valence-level basis set (4-31G)[12] which has been shown[13] to give a very consistent account of hydrogen-bond lengths.[14] The results are summarized in Table I and demonstrate how the equilibrium H···O distances in the reference dimers (see Figure 1) undergo a pronounced contraction (Δ*r* = 0.06–0.07 Å) when the proton-donor oxygen atom is perturbed either by forcing it to adopt the additional role of proton acceptor, or by converting it to a hemiacetal oxygen (vide supra). Thus theory is found to be in close accord with the experimental H···O bond length changes of ~0.1 Å and lends strong support to the hypothesis that the neutron-diffraction data[1] are reflecting intrinsic equilibrium properties of hydrogen bonding and are not artifacts of crystal packing. It should also be noted that the similar Δ*r* values associated with the two types of cooperativity are matched by nearly identical increases (~1 kcal/mol) in calculated hydrogen-bond energy (cf. Tables IA and IB).

As a partial check on the reliability of our theoretical results we have calculated the dimer-to-trimer H···O contraction for water, using both the 4-31G basis (results given in Table I) and the more flexible 6-31G* basis,[15] which reproduces[13c] the