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Theoretical Aspects of the OH···O Hydrogen Bond and Its Role in Structural and Kinetic Phenomena

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Abstract

Ab initio molecular-orbital theory, in conjunction with a flexible atomic-orbital basis set (4-31G), has given a good quantitative account of phenomena associated with the OH···O bond, using methanediol and one or two hydrogen-bonded water molecules as model systems. The calculations and the available crystal structure data both lead to the following conclusions: (1) OH···O bonds involving an anomeric OH donor group are shorter and stronger than those associated with non-anomeric O, and OH groups (whether anomeric or non-anomeric) which are also proton acceptors serve as more effective proton donors; in either case, the H···O bond-length shortening falls in the range 0·07 ± 0·02 Å; (2) although the anomeric OH group can serve as a proton acceptor, its affinity for this role is less than for a non-anomeric O, as inferred by consideration of bond energy and the length of the acceptor H···O bond; (3) the difference in lengths of the two CO bonds in the hemiacetal group bearing the anomeric O atom (O_a) is sensitive to the hydrogen-bonding environment, with variations of up to 0·04 Å being observed; cooperative coupling of proton donor and acceptor functions at O_a occurs at the expense of disproportionation in CO bond lengths; (4) studies of small clusters of water molecules indicate that extended sequential OH···O bonding, with each monomer donating and accepting one proton, yields cooperative shortening of O···O distances and lengthening of the short OH bonds (those involved as proton donors) which can be used to rationalize the limiting magnitudes observed in ice I. In contrast, the branched pentamer has the same O···O separation as the dimer because of the unfavorable double-donor and double-acceptor roles played by the central water molecule.

Introduction

Recent neutron diffraction studies of carbohydrate molecules (Jeffrey & Takagi, 1978; Jeffrey & Lewis, 1978; Ceccarelli, Jeffrey & Taylor, 1981; Jeffrey & Małuszyńska, 1981; Jeffrey, 1982; Jeffrey & Mitra, 1983; Saenger, 1979*a*,*b*; Lindner & Saenger, 1982) have yielded a body of precise crystal structure data pertaining to OH···O hydrogen bonds and have given new impetus to theoretical studies (Newton & Jeffrey, 1977; Tse & Newton, 1977; Newton, Jeffrey & Takagi, 1979). Much of the theoretical work on hydrogen bonding over the past decade has focused on the equilibrium characteristics of prototype systems, such as the dimers obtainable from the simple first-row (NH_3, H_2O, HF) and second-row (PH_3, H_2S, HCl) hydrides (Hankins, Moskowitz & Stillinger, 1970; Del Bene & Pople, 1970; Allen, 1975; Dill, Allen, Topp &

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Pople, 1975; Kollman, 1977; Tse, Newton & Allen, 1980). The data now available from carbohydrate crystal structure analyses provide the opportunity for more sensitive tests of theoretical models through the consideration of subtle differential effects (*e.g.* substituent and cooperative effects and bifurcated bonding) (Hankins, Moskowitz & Stillinger, 1970; Del Bene & Pople, 1970; Tse & Newton, 1977; Newton, Jeffrey & Takagi, 1979; Tse, Newton & Allen, 1980). By extension of the concepts generated from such studies one can address non-equilibrium properties such as vibrational spectra (Curtiss & Pople, 1975; Newton, 1977) and diffusion processes [*e.g.* the dielectric relaxation of ice (Newton, 1982)]. In this paper we present results from a series of *ab initio* calculations which indicate that such phenomena can indeed be analyzed effectively using present-day techniques of computational chemistry in conjunction with concepts of chemical valence theory. In particular, we shall demonstrate the existence of strong correlations among various inter- and intramolecular structural features of hydrogen-bonded clusters, emphasizing the quantitative agreement between the theoretical predictions and the available crystal structure data. The reader is referred to the publications of Schuster, Zundel & Sandorfy (1976) and Kollman (1977) for general reviews on the status of our current understanding of hydrogen bonding.

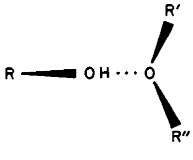
Computational methods

Unless noted otherwise, all the calculations reported here were conventional closed-shell *ab initio* molecular-orbital calculations (Binkley, Whiteside, Hariharan, Seeger, Hehre, Lathan, Newton, Ditchfield & Pople, 1978; Binkley, Whiteside, Krishnan, Seeger, DeFrees, Schlegel, Topiol, Kahn & Pople, 1980). Equilibrium values of geometrical parameters were obtained by minimizing the total molecular energy (Binkley *et al.*, 1980). The molecular orbitals were expanded in various atom-centered orbital basis sets. Three types were employed: (1) a minimal basis (STO-3G) (Hehre, Stewart & Pople, 1969); (2) a split-valence basis (4-31G) (Ditchfield, Hehre & Pople, 1971), in which two basis functions were used to represent each valence atomic orbital, with a single function for the C- or O-atom 1*s* core; and (3) a split-valence basis for C or O which was supplemented with a single set of *d* orbitals (6-31G*) (Hariharan & Pople, 1972).

Methyl-substituent effects

We first review the relatively simple methyl-substituent effect on hydrogen bonding. An understanding of the effect of replacing any of the terminal H atoms in the water dimer with methyl groups is of interest for several reasons. Decisions regarding the ability of simple monomers such as water or methanol to serve as models in more complicated OH···O hydrogen-bonded situations (*e.g.* those occurring in carbohydrate solids) require a knowledge of any significant alkyl-substituent effects. Simulation studies of the liquid properties of water, methanol, and dimethyl ether are being carried out (Jorgensen, 1981), and the pair-wise potential-energy functions upon which these studies depend must reflect any variation in OH···O hydrogen-bond properties associated with the degree of methyl substitution. A previous theoretical study with the STO-3G minimal basis (Del Bene, 1971) suggested that such substituent effects were appreciable and could be understood in terms of a simple charge-transfer model associated with the isolated monomers: *e.g.* replacing H′ with CH_3 in H′OH leads to a depletion of electron density on both atoms of the remaining OH group, which as a result becomes enhanced or inhibited in its ability (relative to H_2O) to serve as a proton donor or acceptor, respectively. In all cases, the resulting OH···O bond strengthening or weakening was accompanied, respectively, by bond shortening or lengthening.

In the course of some model studies related to OH···O hydrogen bonding in pyranoses and pyranosides (Tse & Newton, 1977) we re-evaluated the extent of the CH_3-substituent effect using the larger 4-31G and 6-31G* basis sets, and more recently a thorough study of all linear hydrogen-bonded dimers formed from H_2O, CH_3OH and $(CH_3)_2O$ has been completed (Tse, Newton & Allen, 1980). The dimers are schematically represented as (I):



(R, R′, R″ = H or CH_3)

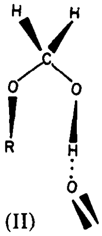
(I)

Both of the extended basis sets (4-31G and 6-31G*) give a similar qualitative picture (although the 4-31G basis systematically exaggerates the strength of the OH···O interactions) and one which is found to differ from the minimal basis (STO-3G) results (Del Bene, 1971), even though all three basis sets imply roughly the same degree of charge separation within the isolated monomers (see above): *i.e.* a CH_3 for H substitution on the average reduces the negative charge on O (inferred from the Mulliken population analysis) (Mulliken, 1955) by ~0·1 e and increases the positive charge on the OH proton by ~0·005 e, an effect which can be attributed to hyperconjugation *via* the resonance structure $H^-CH_2{=}O^+H$. With the extended basis sets, the variations in bond energy (D_e) and equilibrium

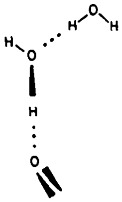
OH···O separation (r_e) are attenuated (r.m.s. variations in D_e and r_e are only ~0·4 kJ mol^{-1} and ~0·01 Å, respectively, compared with values of ~2 kJ mol^{-1} and ~0·03 Å, for the minimal basis) (Tse, Newton & Allen, 1980) and some of the surviving trends are *reversed*, relative to the STO-3G results. Thus, while CH_3 substitution at the acceptor O leads to a shortening and strengthening of the OH···O bond (counter to the STO-3G results), CH_3 substitution at the donor O also yields shortening, but this time accompanied by a weakening of the bond. Furthermore, the effective atomic charges for isolated monomers are seen to be of questionable significance in rationalizing such subtle bonding effects.

Stronger perturbations

Having concluded that the CH_3 group leads to a weak substituent effect in the case of the neutral OH···O hydrogen bond, we turn now to stronger perturbations of the water dimer. Replacing the terminal H atom at the proton donor O with the ROCH$_2$ group generates a hemiacetal (II), which provides a model for the anomeric OH group occurring in aldopyranose sugars (Jeffrey, Pople & Radom, 1972, 1974; Tse & Newton, 1977; Jeffrey, Pople, Binkley & Vishveshwara, 1978) [O_a denotes the anomeric O atom and O_r denotes the O atom which would be a ring atom in the pyranose ring (see Figs. 1 and 2)]. A second type of perturbation arises when the proton-donor O atom serves also as a proton acceptor as in structure (III) (Del Bene & Pople, 1970; Hankins, Moskowitz & Stillinger, 1970; Tse & Newton, 1977).



(II)



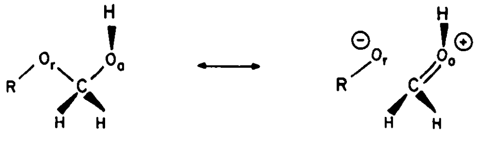
(III)

Both of the above modifications lead to the possibility of cooperative structural and energetic effects since in each case the original OH···O bond and the added functionality can be expected to interact with each other in a non-additive fashion. We first consider the nature of OH···O bonds involving the hemiacetal group (II) and then examine the extent to which the hydrogen-bonding environment can affect the nature of the hemiacetal CO bonds. We then investigate related cooperative effects in hydrogen-bonded clusters of water molecules.

Hydrogen bonding and the hemiacetal group

The anomeric effect

Prior to addressing hydrogen-bond properties we review briefly the intrinsic nature of the hemiacetal group and the anomeric effect. The preference for *gauche* or synclinal (±*sc*) conformations in the RO_rCO_a and O_rCO_aH sequences of the hemiacetal group (II) is a manifestation, respectively, of the anomeric and *exo*-anomeric effect observed in carbohydrates and has been thoroughly analyzed in previous work (Jeffrey, Pople & Radom, 1972, 1974; Jeffrey, Pople, Binkley & Vishveshwara, 1978). While much of the effect may arise from dipolar interactions between the two polar ends of the group, additional stabilization is expected from electronic resonance. Thus for the *ap*,*sc* conformer, where the two entries refer to conformations about the CO_r and CO_a bonds, respectively, and where *ap* denotes a *trans*-staggered or antiperiplanar conformation, we can envision resonance between the following valence structures:



(IV*a*) (IV*b*)

No such resonance is possible for the fully staggered conformation (*ap*,*ap*) due to vanishing of the relevant overlap between the lone pair on O_a (antisymmetric with respect to the CO_aH plane) and the antibonding σ orbital associated with the CO_r group. In the following discussion, we shall specifically consider methanediol (II, R = H), with the +*sc*,+*sc* and *ap*,+*sc* conformations serving as models for α- and β-pyranose sugars, respectively (see Figs. 1 and 2) (Jeffrey, Pople & Radom, 1972). The α- and β-pyranoses are characterized by axial and equatorial CO_a groups, respectively. The *ap*,*ap* conformation of methanediol will also be considered for purposes of comparison.

The electron-deficient nature of the O_aH group in structure (IV*b*) suggests that the anomeric effect might tend to enhance (inhibit) the proton-donor (-acceptor) capability of the O_aH group, relative to that exhibited by simple reference systems such as water or methanol (by contrast, proton accepting at O_r might be enhanced). Such expectations regarding the proton-donor ability are consistent with preliminary model *ab initio* calculations (Tse & Newton, 1977) and also with available neutron diffraction data for pyranose molecules [see experimental crystal structure data cited by Jeffrey & Takagi (1978), Jeffrey & Lewis (1978), Ceccarelli, Jeffrey & Taylor (1981), Jeffrey & Małuszyńska (1981) and Jeffrey (1982)], which indicate that the OH···O bonds with an anomeric proton

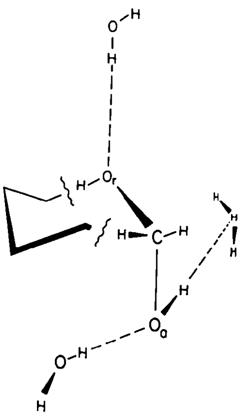


Fig. 1. Model of hydrogen bonding involving the hemiacetal moiety of the α-D-aldopyranose system with $^4C_1$ ring conformation (Jeffrey, Pople & Radom, 1972). For completeness, the framework of the full pyranose ring is indicated schematically, with the wiggly lines demarcating the actual species employed in the model calculations – namely, methanediol in the $+sc,+sc$ conformation ('α-diol'). The subscripts a and r designate 'anomeric' and 'ring' O atoms, respectively.

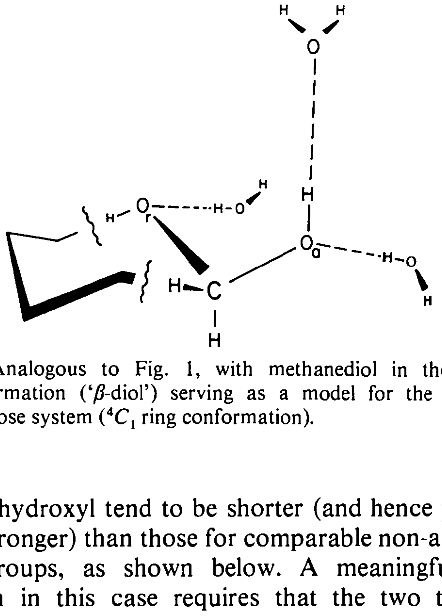


Fig. 2. Analogous to Fig. 1, with methanediol in the $ap,+sc$ conformation ('β-diol') serving as a model for the β-D-aldopyranose system ($^4C_1$ ring conformation).

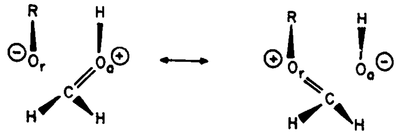
donor hydroxyl tend to be shorter (and hence presumably stronger) than those for comparable non-anomeric OH groups, as shown below. A meaningful comparison in this case requires that the two types of proton-donor group must have the same status with regard to proton accepting (*i.e.* donor only, or combined donor/acceptor) (Jeffrey & Takagi, 1978).

The foregoing discussion underscores the useful role which simple charge-transfer and bonding models may play in predicting structural effects. However, we employ the above resonance arguments in an approximate, qualitative manner and emphasize that their main value lies in suggesting areas worthy of detailed *ab initio* or experimental studies (in the case of a phenomenon as subtle as the methyl-substituent effect we saw above that simple charge models can actually lead to a picture which is qualitatively incorrect).

Structural questions

Previous studies of methanediol or its methoxy derivatives have been limited to (1) optimization of the geometries of the isolated isomers (Jeffrey, Pople & Radom, 1972, 1974; Jeffrey, Pople, Binkley & Vishveshwara, 1978) and (2) partial optimization of the $O_aH\cdots O$ hydrogen bond with fixed methanediol geometry taken from average geometrical parameters for appropriate α- or β-pyranose structures (Tse & Newton, 1977). Only $OH\cdots O$ hydrogen bonds with O_a serving as a proton donor were considered, since O_a was not expected to be an especially favorable proton acceptor, as discussed above. The recent literature has revealed that the O_a atom does occasionally serve as both proton donor and acceptor although the acceptor bonds are appreciably weaker than the O_aH donor bonds (Jeffrey & Takagi, 1978; Jeffrey & Lewis, 1978). Furthermore, the other hemiacetal O atom (O_r) is often found serving as a proton acceptor, with the $O_r\cdots HO$ bonds often comprising the weaker halves of asymmetrical bifurcated bonds (Jeffrey & Małuszyńska, 1981; Jeffrey, 1982). One wishes to understand the extent to which the various $OH\cdots O$ configurations observed in the crystal structure data reflect intrinsic chemical-bonding preferences as suggested by Jeffrey and co-workers (Jeffrey & Takagi, 1978; Jeffrey & Maluszyńska, 1981; Jeffrey, 1982). It is therefore of interest to examine the proton-acceptor capability of both O_a and O_r, as well as extending our understanding of the O_aH proton-donor function.

It is also desirable to ascertain whether the observed differences in CO_r and CO_a bond lengths (Jeffrey, Pople, Binkley & Vishveshwara, 1978) are dependent to some degree on hydrogen-bonding arrangements. For the $ap,\pm sc$ conformation, resonance represented by structure (IV*b*) is consistent with the sign of previously observed (+0·031 Å) and calculated (+0·026 Å) differences relevant to the β-aldopyranoses (Jeffrey, Pople, Binkley & Vishveshwara, 1978) although the relative weight of structure (IV*b*) in the overall wavefunction in unclear. One might reasonably expect more nearly equivalent CO bond lengths in α-pyranoses ($+sc,+sc$), where the resonance structure (IV*d*) might be equal in importance to (IV*c*). Calculations using monomethoxymethanediol as a model for the pyranoses provide a small perturbation of the twofold symmetry in $+sc,+sc$ methanediol but the calculated difference between CO_a and CO_r (0·004 Å) is nearly an order of magnitude less than the similar values which are observed in α- and β-pyranose crystal structures (Jeffrey, Pople, Binkley & Vishveshwara, 1978). This raises the interesting possibility that hydrogen bonding of the $O_aH\cdots O$ type may be the factor which introduces enough of a bias favoring (IV*c*) into the environment of the $+sc,+sc$ conformer so that much of the difference which might exist between the CO bond-length variations in the isolated α- and β-pyranose molecules may be strongly attenuated in hydrogen-bonded crystal structures, as discussed below. On the other hand, the subsequent addition of the proton-acceptor function might nullify this bias since the simultaneous presence of donor and acceptor functions might lead to no net preference for (IV*c*) or (IV*d*). The quantitative extent of such effects can only be ascertained from detailed calculations, which we now describe.



(IV*c*) (IV*d*)

New calculations

We have carried out molecular-orbital calculations (4-31G) for methanediol in several environments: (1) the free molecule; (2) the dimer formed with a water molecule, with O_a serving as a proton donor ($O_aH\cdots O$) or proton acceptor ($O_a\cdots HO$); this 'acceptor-only' situation has apparently not been observed but is considered here as a point of reference; and (3) the trimer formed by adding a proton-donor water molecule to O_a or O_r of the $O_aH\cdots O$ dimer. For brevity, we refer to +*sc*,+*sc* and *ap*,±*sc* methanediol as α-diol and β-diol, respectively, in the following discussion.

Our goal is to calculate the changes in geometry (specifically the OH···O, CO_a, and CO_r bond lengths) as the conformation and hydrogen-bonding environment of methanediol are varied. For the α-diol case (see Fig. 1), the geometry of the free diol and the $O_aH\cdots O$ hydrogen-bonded dimer were completely optimized. Total optimization of the analogous β-diol dimer led to a cyclic hydrogen-bonded structure in which the proton acceptor (water) in the $O_aH\cdots O$ bond was also serving as a proton donor to O_r. While this structure is indeed of interest and undoubtedly relevant to the isolated dimer, it was not felt to be pertinent to the present study since such intramolecular effects are not generally observed in the crystal structure data which we wish to compare with our calculated results. Accordingly, all hydrogen-bonded β-diol structures, as well as all the α-diol structures involving two hydrogen-bonded water molecules (where similar possibilities for cyclic hydrogen-bond formation exist) were optimized with angular constraints.

For the β-diol–water dimer ($O_aH\cdots O$), all *intramolecular* angles for the separate monomers were optimized, and the intermolecular angles were those reported in Table 1* of Tse & Newton (1977), where

Table 1. *Variation in* OH···O *hydrogen-bond lengths and bond energies*

	Non-anomeric donor		Anomeric donor		Difference[a]	
	$r_{H\cdots O}$[b]	D_e[c]	$r_{H\cdots O}$[b]	D_e[c]	$\Delta r_{H\cdots O}$[b]	ΔD_e[c]
(*A*) Donor only[d]						
Calculated	1·88[e]	33	1·80 (α) 1·80 (β)	39 (α) 37 (β)	−0·08	+5·0
Experimental	1·89 (0·07)[f]	–	1·84 (0·07)[g]	–	−0·05	–
(*B*) Donor/acceptor[h]						
Calculated	1·81[i]	44	1·76 (α)[j] 1·74 (β)[j]	42 (α) 40 (β)	−0·06	−3·0
Experimental	1·81 (0·07)[k]	–	1·75 (0·08)[l]	–	−0·06	–
(*C*) Difference (*B* − *A*)						
Calculated	−0·07	+11	−0·05[m]	+3·0[m]		
Experimental	−0·08	–	−0·09	–		

Notes: (*a*) The average α- and β-diol 'anomeric' results subtracted from 'non-anomeric' results. (*b*) Distance in Å. (*c*) Dissociation energy (kJ mol^{-1}) of the dimer ('donor-only' case, relative to the two monomers) or the trimer ('donor/acceptor' case, relative to the dimer and the water monomer). (*d*) Methanol, α-diol, or β-diol serves as the proton donor and a water molecule is the proton acceptor (Figs. 1 and 2). (*e*) As an alternative 'non-anomeric' proton donor we considered the *trans*-staggered (*ap*,*ap*) conformer of methanediol, obtaining values of 1·84 Å and 39 kJ mol^{-1} for $r_{H\cdots O}$ and D_e, respectively, indicating a hydrogen-bond strength intermediate to those represented by methanol on the one hand and the energetically more favorable conformations of methanediol (α- and β-diol) on the other. (*f*) See Ceccarelli *et al.* (1981; Table 4, entry 4, sample 2). The estimated standard deviations associated with the experimental data are given in parentheses. (*g*) An average based on eight available structures of the types (I*B*) and (II*B*), as defined by Jeffrey & Takagi (1978): four neutron diffraction structures (Takagi & Jeffrey, 1979; Table 4, types *F* and *S*) and four corrected X-ray structures (Jeffrey & Takagi, 1978; Table 3); α-D-galactose was excluded since its $O_aH\cdots O$ bond is strongly bent (Jeffrey & Shiono, 1977). Equal weight was given to each structure. β-L-Lyxose was included in this set; although it may formally be considered as a donor/acceptor, the acceptor function at the anomeric O involves a very weak ($r_{H\cdots O}$ = 2·11 Å), bent (∠OH···O = 146°) interaction which is a component of a bifurcated hydrogen bond (Nordenson, Takagi & Jeffrey, 1978). (*h*) The acceptor O in the case of α- or β-diol is the 'anomeric' O atom (O_a). For comparison we note that if the other hemiacetal O atom (*i.e.* the 'ring' atom, O_r) serves as the acceptor (see Figs. 1 and 2) the original $O_aH\cdots O$ bond lengths are unchanged (Δr <0·01 Å) and the new $H\cdots O_r$ hydrogen bonds are relatively weak: r = 1·89 Å, D_e = 32 kJ mol^{-1} for the α-diol and r = 1·92 Å, D_e = 27 kJ mol^{-1} for the β-diol. (*i*) Both OH···O distances are the same to within 0·01 Å (Tse & Newton, 1977). (*j*) The $H\cdots O_a$ distances are 1·82 Å (α-diol) and 1·84 Å (β-diol). (*k*) Ceccarelli, Jeffrey & Taylor (1981; Table 4, entry 4, sample 1). (*l*) An average based on six available structures of type (I*A*), as defined by Jeffrey & Takagi (1978): four neutron structures [Takagi & Jeffrey (1979; Table 4, type I) and Gress & Jeffrey (1977)] and the corrected X-ray structures of β-D-galactose (Jeffrey & Takagi, 1978) and α-D-mannose (Jeffrey & Lewis, 1978). Equal weighting was given to each structure. (*m*) Based on the average of the results for α- and β-diols.

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* Note that the symbols α and β in this table are incorrect as they stand and should be interchanged.

the conformation about the H···O bond (denoted φ) and the angle between the H···O vector and the plane of the proton acceptor (denoted θ) were optimized, with other angles maintained at reasonable values based on full optimization for dimers of water and methanol (Dill, Allen, Topp & Pople, 1975; Kollman, 1977; Tse, Newton & Allen, 1980). In particular, the constraint of a linear $O_aH\cdots O$ bond prevents the formation of cyclic structures extraneous to the present study, as noted above.

In the largest clusters (*i.e.* the trimers) an additional, fully optimized proton-donor water molecule was added (either at O_a or O_r, as in Figs. 1 and 2) to the fully (α) or partially (β) optimized methanediol–water dimers (as defined above), with the new intermolecular angles based on the analogous values for the optimized water dimer, including linear OH···O, $\varphi = 180°$ and $\theta = \pm 40°$.*

Subject to the above *angular* constraints, *all* bond distances (H···O as well as intramolecular bonds) were fully optimized for *all* clusters considered in this study. The various calculated OH··O and CO distances are summarized in Tables 1 and 2, respectively (see also Figs. 1 and 2). The new results are completely consistent with those from the earlier similar calculations (Tse & Newton, 1977; Jeffrey, Pople & Radom, 1972) but provide a much more detailed and extensive probing of structural features

Table 2. *Effect of* $O_aH\cdots O$ *bonding on hemiacetal* CO *bond lengths*

Status of O_a	r_{CO}^(a)^ (Å) CO_r	CO_a	Δr_{CO}^(b)^ (Å)
(*A*) α-D-Aldopyranoses			
Calculated (α-diol)			
no H bond	1·410	1·410	0·000
donor only^(c)(d)^	1·423 1·432	1·398 1·393	0·025 0·039
donor/acceptor	1·417	1·406	0·011
Experimental^(e)^			
donor only	1·429	1·396	0·034 (0·009)
donor/aceptor	1·415	1·409	0·010 (0·012)
(*B*) β-D-Aldopyranoses			
Calculated (β-diol)			
no H bond	1·422	1·398	0·024
donor only^(c)(d)^	1·429 1·437	1·391 1·390	0·038 0·047
donor/acceptor	1·424	1·397	0·027
Experimental^(e)^			
donor only	1·433	1·383	0·050^(f)^
donor/acceptor	1·424	1·392	0·032 (0·010)

Notes: (*a*) r_{CO} denotes the two CO bond lengths in the hemiacetal group of the pyranose ring; the calculations are based on methanediol and its hydrogen-bonded complexes with one or two water molecules (see Figs. 1 and 2). (*b*) $r_{CO_r} - r_{CO_a}$; the estimated standard deviations for the experimental data are given in parentheses. (*c*) The first row pertains to the methanediol–water dimer; the second row contains results based on addition of a proton-donor water at the O_r atom of the original dimer, thus maintaining the donor-only status of O_a. (*d*) Analogous calculations with the *ap,ap* methanediol molecule yield 1·413, 1·394 and 0·019 Å for r_{CO_r}, r_{CO_a} and Δr, respectively, compared to a value of 1·406 Å for the two equivalent bonds in the absence of the H_2O molecule. The calculated CO bond length of methanol changes from 1·430 to 1·423 Å when it forms an OH···O bond to water with water serving as the acceptor. (*e*) Taken from tabulations in Jeffrey, Pople, Binkley & Vishveshwara (1978). These data were supplemented with neutron diffraction results for β-D-fructose (Takagi & Jeffrey, 1977), α-L-sorbose (Nordenson, Takagi & Jeffrey, 1979), β-D-L-arabinose (Takagi, Nordenson & Jeffrey, 1979), β-maltose monohydrate (Gress & Jeffrey, 1977), α-D-glucose (Brown & Levy, 1979), α-L-xylose (Takagi & Jeffrey, 1979), and β-L-lyxose (Nordenson, Takagi & Jeffrey, 1978). The relevant information regarding the donor-only or donor/acceptor nature of each anomeric OH group is given by Jeffrey & Takagi (1978) and by Jeffrey & Lewis (1978) as well as in the original literature references cited above. See footnote (*g*) in Table 1 concerning the classification of β-L-lyxose. (*f*) Based on a single data point [β-D-glucose; see footnote (*e*) and Jeffrey, Pople, Binkley & Vishveshwara (1978)].

Results

OH···O *bonds*

We deal first with the OH···O data in Table 1. Both the theoretical and experimental data convey the same qualitative and quantitative picture. Relative to the non-anomeric, donor-only OH group, we find that either the *change* to an anomeric O or the *addition* of the proton-acceptor function leads to a *shortening* of the OH···O bond by 0·07 ± 0·02 Å: *i.e.* the proton-donor OH···O bond is significantly enhanced when it occurs in conjunction with either the anomeric effect or the proton-acceptor function. While both of these effects have been predicted theoretically (Del Bene & Pople, 1970; Hankins, Moskowitz & Stillinger, 1970; Tse & Newton, 1977), only the latter effect has been unequivocally resolved in previous analyses of the experimental data (Ceccarelli *et al.*, 1981). Nevertheless, the sample of presently available data which forms the basis for the experimental values in Table 1 suggests that there is in fact a resolvable difference between the anomeric and non-anomeric OH proton-donor capability. Our conclusions in this regard are consistent with those of Ceccarelli *et al.* (1981). These authors, limiting themselves to a sample of seven anomeric neutron diffraction data points (a subset of that employed here), found no significant distinction between anomeric and non-anomeric OH···O distances. However, they combined data pertaining to donor-only and donor/acceptor situations. To the extent that the statistical *t* test is valid, we find that for the donor/acceptor cases, the mean values given in Table 1 for anomeric donor *vs* non-anomeric donor can be distinguished with 91% confidence. The corres-

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* Because the clusters in the present study do not have the plane of symmetry present in the optimal water dimer, $\theta = 40°$ is not equivalent to $\theta = -40°$. For cases where O_a serves as proton acceptor similar results are obtained for either sign (Figs. 1 and 2 and Tables 1 and 2 correspond to the choice which yields the lowest energy). For the α-diol, the lowest-energy O_r-acceptor structure corresponds to another case of strong cyclic hydrogen bonding (with the proton-accepting water), and we therefore adopted the other sign of θ (as in Fig. 1). For the β-diol, only one sign of θ is feasible, since the other sign leads to severe steric crowding due to the presence of the proton-accepting water molecule (see Fig. 2).

ponding comparison for donor-only cases, where the data are less abundant, can only be made at the 65% confidence level.

In the case of the non-anomeric OH group, the cooperativity between donor and acceptor functions causes the formation of the second hydrogen bond to be accompanied by an energy lowering 11 kJ mol^{-1} greater than that from the initial dimer formation. *Both* of the H···O bonds in the trimer have the same, short distance (1·81 Å).

Let us now examine the ability of the anomeric O atom (O$_a$) to accommodate a proton acceptor. Clearly, the theoretical and experimental data indicate that H···O$_a$ bonds can be formed [six of the 14 experimental data points in our sample (Table 1) provide examples of this]. Nevertheless, the H···O$_a$ bonding is relatively weak in several respects, as initially anticipated [Tse & Newton (1977); see also Takagi & Jeffrey (1978, Table 4)]. First we consider the donor-only *vs* acceptor-only situation. The latter case (not included in Table 1) yields much longer ($r_{\mathrm{H}\cdots\mathrm{O}}$ = 1·9 Å) and weaker (D_e = 32 kJ mol^{-1}) bonds than for the donor-only case. Secondly, the energy associated with adding the H···O$_a$ interaction to the initial donor-only O$_a$H···O bond is only 3·0 kJ mol^{-1} greater than the original dimer energy (*cf.* 11 kJ mol^{-1} for the non-anomeric case) and while the donor/acceptor combination is cooperative in the sense that the initial O$_a$···O separation decreases markedly, the new acceptor bond (H···O$_a$) is relatively long (1·83 Å, based on the average for α-diol and *β*-diol, footnote *j*, Table 1). Experimentally, the average H···O$_a$ separation for the six donor/acceptor cases included in Table 1 is 1·89 Å, with an estimated standard deviation of 0·09 Å.

Turning to the other hemiacetal O, we note that O$_r$ in the O$_a$-donor-only dimer has a relatively low affinity as a proton acceptor, as inferred from the length (1·90 Å) and strength (29 kJ mol^{-1}) of the bonds formed (based on averages for the α- and *β*-diol conformers, footnote *h*, Table 1). Furthermore, the formation of H···O$_r$ bonds has little effect on the O$_a$H···O bond lengths.

There is generally good absolute agreement between the experimental and calculated OH···O distances in Table 1. This situation must be considered somewhat fortuitous since the 4-31G basis typically underestimates OH···O distances [*e.g.* by 0·1 Å for water or methanol dimers (Tse, Newton & Allen, 1980)]. It is to be emphasized, however, that our major conclusions about OH···O bonds rest primarily on *relative* bond lengths and are not expected to be strongly affected by systematic errors of the type just noted (Tse & Newton, 1977).

CO *bonds*

As anticipated above, Table 2 reveals that the CO$_a$ and CO$_r$ bond lengths are strongly dependent on the hydrogen-bonding environment. We find that the maximum disproportionation of CO bond lengths (with $r_{\mathrm{CO}_a} < r_{\mathrm{CO}_r}$) is achieved when the O$_a$H group acts as a proton donor, but not as acceptor; the OH···O bond provides the bias necessary to offset the local symmetry in the α-pyranoses and reinforces the intrinsic CO bond-length differences in the *β*-pyranoses. We also note that these tendencies are enhanced when O$_r$ serves as a proton acceptor, whereas addition of the proton-acceptor function at O$_a$ attenuates the difference in CO$_a$ and CO$_r$ bond lengths. It thus appears as though the cooperativity associated with proton-donor and -acceptor functions at the anomeric O, as discussed in the previous section, occurs somewhat at the expense of the electronic resonance and consequent CO bond-length variation associated with structures (IV*b*)–(IV*d*).

Absolute agreement between calculated and experimental CO bond lengths and Δr values is good. The significance of differences in mean experimental Δr values can be estimated in terms of suitable *t* tests. For the case of donor-only *vs* donor/acceptor, the confidence levels are 99·7% (α-pyranoses) and 82% (*β*-pyranoses). For the α-pyranose *vs* *β*-pyranose comparisons, the confidence levels are 98% (donor/acceptor) and 85% (donor-only). Since the total sample includes only 18 data points, a larger set of experimental data is desirable for the purpose of confirming these preliminary conclusions. Nevertheless, we have provided consistent theoretical and experimental evidence that the relatively weak intermolecular bonds defining the hydrogen-bonding environment of a hemiacetal group exert an appreciable influence on the length of the strong intramolecular hemiacetal CO bonds: *i.e.* variations of up to 0·040 Å in Δr are observed.

An interesting test of our theoretical understanding of variations in CO bonding is provided by calculations in which the O$_a$H group serves only as a proton acceptor (see also comments above regarding the H···O$_a$ bond in this case). As one might anticipate from a consideration of valence structures (IV*c*) and (IV*d*), the acceptor-only situation leads to a *shortening* of CO$_r$ relative to CO$_a$ (by 0·007 Å). It was noted above that the acceptor-only anomeric O has not been observed in the available crystal structure data. Nevertheless, we emphasize that the one known example of an α-pyranose in which CO$_r$ is *shorter* than CO$_a$ (see Jeffrey, Pople, Binkley & Vishveshwara, 1978) corresponds to a case (α-D-mannose) where the acceptor O$_a$···H bond is quite short (1·81 Å) and the donor function is bifurcated and relatively weak (r_{O_a}H···O = 1·99 and 2·40 Å) (Jeffrey & Lewis, 1978), thus at least approaching the limiting situation represented in the acceptor-only model calculation.

Finally we note that restricting the free methanediol molecule to the high-energy *ap,ap* conformation yields equilibrium CO bond lengths which are actually slightly *shorter* than those for the +*sc*, +*sc* conformation [1·406 Å *vs* 1·410 Å (Jeffrey, Pople & Radom, 1972)] in spite of the fact that resonance structures like (IV*b*)–(IV*d*), involving the O π lone-pair orbital (antisymmetric with respect to the COH plane), are expected to have zero weight in the case of the *ap*,*ap* conformation. Inspection of the CO_a overlap populations, however, reveals that while the CO_a π contribution is negative for the *ap*,*ap* case, there is a positive contribution associated with in-plane $p\pi$–$p\pi$ overlap, comparable in magnitude (0·10) to the positive out-of-plane $p\pi$–$p\pi$ values found for the +*sc*,+*sc*, and *ap*,±*sc* conformations (0·08). The effect of OH···O hydrogen bonding on the CO bond lengths of the *ap*,*ap* conformer is about the same as that for the two more energetically favored structures (+*sc*,+*sc* and *ap*,±*sc*). By comparison, the CO bond length of methanol is calculated to decrease by only 0·007 Å when it forms an OH···O bond as a proton donor to water.

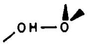
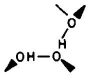
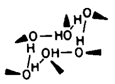
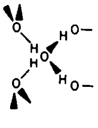
Cooperative OH···O bonding in water clusters

To complete the discussion of cooperative interactions among OH···O bonds, we present some new results for small clusters of water molecules which serve to supplement the earlier minimal basis results of Del Bene & Pople (1970). The contraction of the equilibrium O···O separation (r_e) in ice I (2·75 Å) (Eisenberg & Kauzmann, 1969), relative to that in the gas-phase dimer (2·96 Å) (Dyke, Mack & Muenter, 1977; Newton & Kestner, 1982), and the corresponding increase in the binding energy per water molecule [$D_e = 60{\cdot}9$ kJ mol^{-1} in ice (Whalley, 1973) *vs* a quantity only a third of this for the dimer (Curtiss, Fruip & Blander, 1979)] constitutes a striking example of hydrogen-bond cooperativity. It is of interest to understand how rapidly the O···O separation in small clusters approaches the limiting value observed in ice. We therefore consider a sequence of small clusters, $(H_2O)_n$, where n ranges from 2 to 6, as indicated in Table 3. The O···O distances have been optimized by minimizing the molecular-orbital (4-31G) energy, constraining all O···O separations to be equal. Cooperativity leads to a shortening of 0·08 Å in going from dimer to trimer (Tse & Newton, 1977) and an additional shortening of 0·06 Å is exhibited by the cyclic hexamer (relative to the linear trimer). The hexamer $r_{O\cdots O}$ value is thus estimated to be within 0·1 Å of the value for ice I. This is not surprising since the 'chair' hexamer is an important structural component of ice I (Eisenberg & Kauzmann, 1969). An alternative model for ice – namely the ice-like pentamer, in which a central water is tetrahedrally surrounded by four OH···O bonded neighbors – yields the same O···O distance as the dimer. This, of course, points to another important feature exhibited by ice I: namely, the competition between energetically favorable trimers in which the central water serves as a donor and acceptor (*DA*, see structure III) and unfavorable trimers in which the central water is a double donor (*DD*) or double acceptor (*AA*) (Kollman, 1977; Hankins, Moskowitz & Stillinger, 1970). Table 3 indicates the relevant ratios of dimers and trimers to monomers, and also the ratio of unfavorable (*DD* + *AA*) to favorable (*DA*) trimers for the different clusters.

In the sequence dimer–trimer–hexamer the ratios of nearest-neighbor dimers and favorable (*DA*) trimers to monomers increase monotonically and no unfavorable (*DD*,*AA*) trimers are involved. The branched pentamer has a greater dimer/monomer ratio than for the dimer itself, but the fact that one third of the trimers are unfavorable leads to the result of no net change in O···O separation relative to the dimer. Although ice I has the same trimer ratio (unfavorable/favorable) as the pentamer, it has much greater ratios of dimers and trimers to monomers as well as having larger cooperative sequences such as the cyclic hexamer discussed above. These factors contribute to the large cohesive energy and the large negative value of Δr observed in ice.

Corresponding to cooperative O···O contraction, one also expects weakening and lengthening of the short OH bonds in the OH···O hydrogen linkages. Table 4 displays the results for monomer, dimer, and hexamer. The calculated OH force constants reflect the expected red shift in the hydrogen-bonded OH stretching frequency. In the hexamer, r_{OH} is about 0·02 Å greater than in the monomer, and we do not expect the corresponding change in ice I to be much greater than this. An extrapolation of the calculated data to the limiting case of ice I can be obtained as follows. Assuming that the lengthening of hydrogen-bonded OH bonds in water clusters is proportional to the corresponding decrease in O··O separation (relative to the dimer) and noting that the hexamer calculation yields two thirds of the limiting contraction (0·21 Å) observed in ice I (see Table 3), we estimate a total r_{OH} increase of 0·026 Å in going from the dimer to ice. Adding to this the calculated difference of 0·005 Å between monomer and dimer, and employing the monomer r_e value of 0·957 Å (Kuchitsu & Morino, 1965), we finally obtain an estimate of 0·998 Å for r_e in ice. This value is lower than the value of 1·01 Å obtained from neutron crystal data (Peterson & Levy, 1957); however, the latter value includes the effects of zero-point averaging and is thus expected to be greater than r_e by at least 0·01 Å due to anharmonicity in the OH stretching mode (Kuchitsu & Morino, 1965; Sceats & Rice, 1979; Sceats, Stravola & Rice, 1979). Whalley (1974) has emphasized the difficulties in rationalizing an OH bond length as long as 1·01 Å in ice I. The model calculations presented here suggest that stretching the OH bonds to this extent may be energetically feasible as a result of the cooperative enhancement associated with multiple sequential OH···O bonds. The fact that OH elonga-

Table 3. *Hydrogen-bonded water clusters*

	Cluster	Symmetry	$\Delta r_{O\cdots O}$[a] (Å)	Dimers/H_2O[b]	Trimers/H_2O[c]	$(DD + AA/DA)$[d]
(*A*) Linear		C_s	—	1/2	—	—
		C_1	−0·08[e]	2/3	1/3	0
(*B*) Cyclic		S_6[f],[g]	−0·14	1/1	1/1	0
(*C*) Branched		C_{2v}[f],[h]	0·0	4/5	6/5	1/2
	Ice I		−0·21[i]	2/1	6/1	1/2

Notes: (*a*) Change in equilibrium O···O separation relative to that for the dimer, based on molecular-orbital results (4-31G), except for ice [see footnote (*i*)]. (*b*) Ratio of nearest-neighbor (*NN*) dimers to monomer units. (*c*) Ratio of sequential trimers (*i.e.* formed from adjacent hydrogen-bonded water molecules) to monomer units. (*d*) Ratio of trimer types. *DA*, *DD* and *AA* refer to sequential trimers in which the central water serves, respectively, as a donor/acceptor, a double donor, and a double acceptor. (*e*) Tse & Newton (1977). (*f*) All OOO, HO···O and HOH bond angles are constrained to be tetrahedral. (*g*) All peripheral OH bonds in the 'chair' structure are equatorial. (*h*) Each *NN* dimer unit has the optimal dimer conformation [see footnote (*e*)]. (*i*) Experimental value based on O···O separations for the gas-phase dimer (Dyke, Mack & Muenter, 1977) and ice I at 0 K (Eisenberg & Kauzmann, 1969). The experimental r_0 value for the dimer (2·98 Å) corresponds to an r_e value of 2·96 Å (Newton & Kestner, 1982).

Table 4. *Calculated* (4-31G) *bond lengths and force constants for hydrogen-bonded* OH *bonds*

The monomer was assigned ∠HOH = $\cos^{-1}(-1/3)$ and the optimal r_{OH} value was determined to be 0·952 Å. The larger clusters are based on rigid monomers except for the hydrogen-bonded OH bonds, with OOO and HO···O angles maintained at $\cos^{-1}(-1/3)$, and ∠OH···O kept at 180°. The point-group symmetry is the same as in Table 3.

Cluster	r_{OH} (Å)	k_{OH} (nN Å^{-1})
H_2O	0·952	90[a]
$(H_2O)_2$	0·957	86[b]
$(H_2O)_6$	0·974	69[b]

Notes: (*a*) The average of the symmetric and antisymmetric stretching force constant. (*b*) Second derivative with respect to the hydrogen-bonded OH bond, with the OO separation kept at equilibrium values (see Table 3).

tion appears to be less pronounced in ice II and ice IX may be related in part to the departures from linearity in the OH···O bonds exhibited by these ices (Kamb, Hamilton, La Placa & Prakash, 1971; La Placa, Hamilton, Kamb & Prakash, 1973).

Force constants based on 4-31G-level calculations are generally greater than experimental values. Nevertheless, their systematic behavior has been shown to provide good correlations with experimental vibrational frequencies (Curtiss & Pople, 1975; Newton, 1977). In the present context, we note that the ratio of calculated force constants for H_2O and $(H_2O)_6$ is very similar to the square of the ratio of OH stretching frequencies observed for free H_2O and ice (Fletcher, 1970), *i.e.* ~3/4. Thus to the extent that effective masses can be assumed to cancel in the frequency ratio, we may conclude that the cyclic hexamer, while clearly not a complete model for ice (see above), yields a red shift comparable to that observed in ice I.

Summary and conclusions

Ab initio molecular-orbital theory, employed in conjunction with a flexible atomic-orbital basis set (4-31G), has given a good quantitative account of a variety of phenomena associated with the OH···O bond using methanediol and one or two hydrogen-bonded water molecules as model systems. The calculations and the available crystal structure data both lead to the following conclusions: (1) OH···O bonds involving an anomeric OH donor group are shorter and stronger than those associated with non-anomeric O, and OH groups (whether anomeric or non-anomeric) which are also proton acceptors serve as more effective proton donors; in either case, the H···O bond-length shortening falls in the range 0·07 ± 0·02 Å; (2) although the anomeric OH group can serve as a proton acceptor, its affinity for this role is less than that of a non-anomeric O atom, as inferred by consideration of bond energy and the length of the acceptor $H\cdots O$ bond; (3) the difference in lengths of the two CO bonds in the hemiacetal group bearing the anomeric O atom (O_a) is quite sensitive to the hydrogen-bonding environment, with variations of up to 0·04 Å being observed; cooperative coupling of proton-donor and -acceptor functions at O_a is seen to occur at the expense of disproportionation in CO bond lengths; (4) studies of small clusters of water molecules indicate that extended sequential $OH\cdots H$ bonding, with each monomer donating and accepting one proton, yields co-operative shortening of $O\cdots O$ distances and lengthening of the short OH bonds (those involved as proton donors) which can be used to rationalize the limiting magnitudes observed in ice I. In contrast, the branched pentamer has the same $O\cdots O$ separation as the dimer because of the unfavorable double-donor and double-acceptor roles played by the central water molecule.

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