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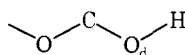
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Theoretical Observations on the Structural Consequences of Cooperativity in H...O Hydrogen Bonding

Sir:

Neutron diffraction studies on three methyl pyranosides reported in the preceding communication¹ 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,

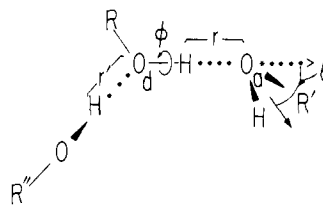


Figure 1. Schematic representation of hydrogen-bonded dimers and trimers, indicating H...O bond lengths (r, r'), the angle (θ) between the H...O vector and the plane of the proton acceptor $R'O...H$, and the torsion angle (ϕ) between the bisector of the proton acceptor bond angle ($R'O...H$) and the $O...R$ 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 $\phi = 180^\circ$ and the arrow (\curvearrowright) shows the sense of rotation of $O...R$ 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.

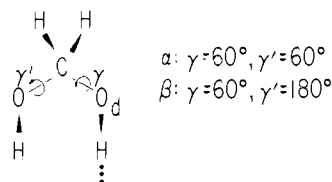


Figure 2. Methanediol as a model for the hemiacetal or anomeric proton-donor oxygen atom (O_d). The conformations designated as α and β are models for α and β pyranose rings, respectively (cf. ref 3). The structure displayed corresponds to the α conformation. The torsion angles γ and γ' refer to the 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 data²⁰ ($r_{CO_2} = 1.39$ Å; $r_{CO} = 1.43$ Å; $\angle CO_2 = 112^\circ$ (α), 107° (β)) or energy optimization ($\angle HCH = 110^\circ$). The bisectors of $\angle HCH$ and $\angle CO_2$ coincide and the corresponding planes are perpendicular (by constraint).

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}

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 effect³), 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 shown¹³ 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 ($\Delta r = 0.06$ - 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 data¹ are reflecting intrinsic equilibrium properties of hydrogen bonding and are not artifacts of crystal packing. It should also be noted that the similar Δr 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

Table I. Influence of Cooperative Interactions on the OH...O Bond Length (r)^a

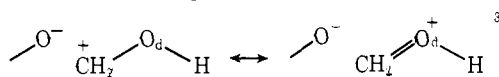
Monomer	A. Interaction between the Proton-Donor and Proton-Acceptor Function ^b				Trimer		
	r	θ	ϕ	E^c	$\Delta r^{d,e}$	$\Delta r'^{d,f}$	E^c
Methanol ^{e,f}	1.86	30°	180°	8.1	-0.06	-0.05	9.1
Water ^{e,h}	1.89	36°	180°	8.1	-0.08	-0.08	9.3

Donor	B. Interaction between the Proton-Donor Function and the Gauche Effect ⁱ			E^c
	r	Δr^j	θ	ϕ
Methanol ^k	1.88	—	36°	180°
Methanediol ^l				
β	1.82	-0.06	28°	-112°
α	1.81	-0.07	43°	-119°

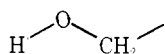
^a The geometrical parameters listed (r, θ, ϕ ; see Figure 1 and 2) are the equilibrium values. Units are Å (distance) and kcal/mol (energy). All results are based on experimental monomer geometries and the 4-31G basis unless otherwise specified. The H...O distances are presented (as opposed to the O...O distances) so as to allow direct comparison with the data of ref 1; these data are based on hydrogen bonds which depart somewhat from perfect linearity. As noted in ref 14, the 4-31G r values are expected to be underestimated by ~5%. ^b See Figure 1 for schematic geometry. The optimal dimer angles (θ, ϕ) were employed in constructing the trimer structures. ^c Energy per hydrogen bond (average value, for case of trimers). ^d Δr and $\Delta r'$ are, respectively, the r and r' values relative to the dimer r value. ^e R,R',R'' = CH₃ (see Figure 1). For monomer geometry see ref 21. ^f See ref 17. ^g R,R',R'' = H (see Figure 1). For monomer geometry see ref 21. ^h The dimer results were reported in ref 13b. ⁱ Based on a dimer model (R''OH not included; see Figure 1). Water (R' = H) served as the proton acceptor molecule. ^j Δr is the change in r relative to the methanol value. ^k R = CH₃ (see Figure 1). ^l R = HOC(H₂) (see Figure 1). The α and β conformations are defined in Figure 2.

experimental¹⁶ O...O distance of the dimer. The Δr values calculated with the two basis sets differ only by ~0.01 Å. The results for the water and methanol polymers merit two further comments. First, the 0.10 Å shortening originally predicted for the trimer with the minimal STO-3G basis^{4a} turns out to be in reasonable agreement with the larger basis set calculations even though the absolute O...H distances are greatly underestimated by the smaller basis. Secondly, comparison of the results for methanol and water dimers (Table IA) reveals an interesting situation in which a modest chemical change (methyl substitution) causes an appreciable shift (0.03 Å) in H...O distance without a corresponding change in hydrogen-bond energy.¹⁷

The similar structural as well as energetic consequences of the two types of cooperativity dealt with in the preceding sections are perhaps intuitively understandable once one recognizes the simple electronic basis of the two effects. The donor-acceptor cooperative effect has previously been analyzed^{4,5,7,8} in terms of intramolecular charge polarization: when a monomer ROH serves as a proton acceptor its own proton loses electron density (~0.02 electrons for R = H or CH₃), and hence it becomes a more effective proton donor in an additional hydrogen bond. In the case of the hemiacetal or anomeric oxygen (O_d), the key factor is a significant resonance admixture of the following two valence structures,



The latter structure, which leads to the preference for the gauche conformation and to an intramolecular CO bond shortening,^{3b,3c} also implies an appreciable depletion of charge at the anomeric proton, found from population analysis to be ~0.02 electrons relative to the methanol hydroxyl proton, i.e., roughly the same as the proton charge shift experienced by methanol when it becomes a proton acceptor. It is clear that a cooperative relationship would exist between the conjugation illustrated above and proton donation by the anomeric oxygen. This effect is much larger than one would expect merely on the basis of the sigma inductive effect of an



group attached to the donor oxygen.¹⁸ Confirmation of this analysis is provided by the fact that the trans-staggered conformer ($\gamma, \gamma' = 180^\circ$) of methanediol, in which the conjugation is suppressed, yields only a very small (0.01 Å) H...O contraction relative to methanol.

Our theoretical studies lead to additional structural predictions regarding the role of the anomeric oxygen in intermolecular hydrogen bonding—namely, that both α and β pyranoses (see Figure 2) should exhibit similar H...O distances when serving as proton donors (to a given type of acceptor), and that the anomeric oxygen atom should be a relatively poor proton acceptor. The latter prediction is consistent with the fact that, in a set of 12 simple pentoses and hexoses for which x-ray or neutron crystal structures are available, the anomeric oxygen serves as a proton acceptor in only three cases, and the hydrogen bonds in these cases are weak ($r_{\text{H...O}} > 2.0$ Å).²²

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Excited State Relaxation and Chromium(III) Photochemistry

Sir:

Implicit in discussions of Cr(III) photochemistry has been the assumption that a unique chemical species is involved in all of the photochemical and photophysical processes.¹ At any instant, a variety of solvent arrangements obtains about a transition metal complex. If the interconversion rates between the solvates are rapid compared to the reaction rate, it is appropriate to speak of a single solvated chemical species. Multiple emission decays observed from $\text{Cr}(\text{CN})_6^{3-}$ in rigid glass solvents were ascribed to different environments, but, as the solvent became fluid, the nonexponentiality disappeared, as would be expected if a single species were present.² We now present evidence for multiple solvates of $\text{Cr}(\text{CN})_6^{3-}$ in H_2O at room temperature with interconversion rates less than 10^7 s^{-1} .

${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission was excited at several wavelengths (Figure 1) by an Avco C-950 N_2 laser or tuned dye lasers (BBOT and POPOP) pumped by the N_2 laser. The decay profiles were monitored by a C-31034 photomultiplier with a 50Ω load and a Tektronix 7904-7A19 oscilloscope. The $\text{Cr}(\text{CN})_6^{3-}$ ${}^2\text{E}$ lifetimes at different excitation wavelengths are shown in Figure 2 for two solvents, water, and 80% (v/v) glycerol-water. The decays were all exponential in the time intervals that could be used ($\sim 2\tau$). The emission spectra, recorded with a Jarrell-Ash 0.25-m monochromator (without slits) and a PAR Model 160 boxcar integrator, are also dependent on the excitation wavelength (Figure 3).

Since the major changes in lifetimes occur upon excitation in the red edge of the ${}^4\text{T}_2 \leftarrow {}^4\text{A}_2$ absorption band, the possibility that impurities and/or photoproducts were responsible

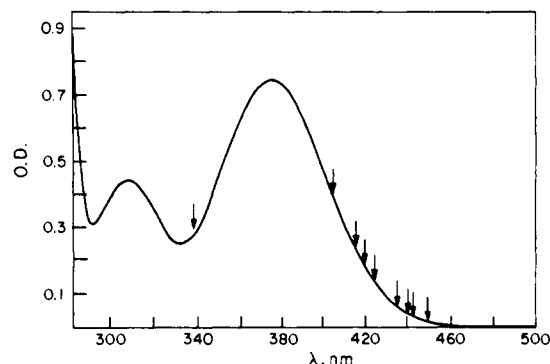


Figure 1. $\text{Cr}(\text{CN})_6^{3-}$ absorption spectrum (from ref 3).

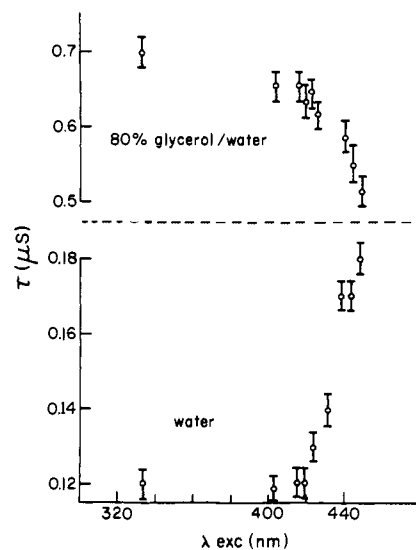


Figure 2. ${}^2\text{E}$ lifetimes in different solvents as a function of excitation wavelength.

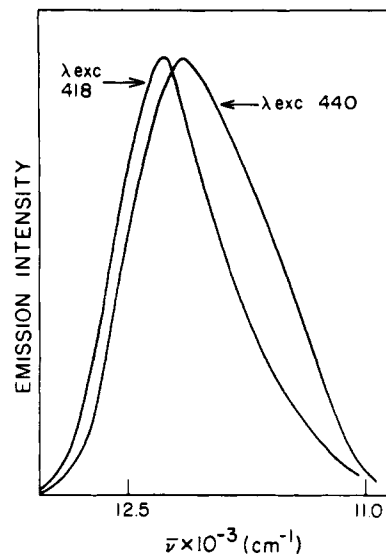


Figure 3. $\text{Cr}(\text{CN})_6^{3-}$ emission spectra in water for different excitation wavelengths.

for the effect was carefully examined. The absorption spectrum of twice-recrystallized $\text{K}_3\text{Cr}(\text{CN})_6$ (City Chemical Corp., Electronic Grade) agreed very well with the published spectrum,³ and the lifetimes were unchanged upon repeated recrystallization from water. The lifetime at 337 nm was the same after 1 and 80 laser pulses. Finally, any impurity or