Comparison of Cooperativity in CH···O and OH···O Hydrogen Bonds

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Received: April 2, 2004; In Final Form: July 22, 2004

The ability of one H-bond in a chain to affect others is assessed by comparing the CH···O bonds in $(H_2CO)_n$ and $(HFCO)_n$ to the OH···O bonds in $(H_2O)_n$. Both sorts of interactions grow stronger, and the intermolecular distances shorter, as the number of monomers in the chain increases. The degree of cooperativity is generally proportional to the strength of the H-bond, although the CH···O bonds in $(HFCO)_n$ display a disproportionately high degree of cooperativity. The cooperativity of OH··O and CH···O bonds is similar also with respect to electron density loss from the bridging hydrogen atom, and the amount of charge transferred from the proton-acceptor molecule to the donor. The covalent CH bonds are shortened upon H-bond formation, and the associated stretching frequencies undergo a blue shift, both opposite to what is observed in OH···O systems. These properties exhibit little indication of cooperativity for CH, while the OH bond stretches and red shifts of the OH frequencies are enhanced as *n* increases. NMR chemical shifts of the bridging proton likewise suggest that CH···O bonds are much less cooperative than OH···O. Cooperativity is reduced in all systems as the dielectric constant of a surrounding solvent is enhanced.

Introduction

The prevalence and importance of the hydrogen bond has made this molecular interaction into one of the most studied phenomena over the years.[1−4] This work has led to a suite of trademark properties of the H-bond that include a certain range of energetic strength, and geometric and spectroscopic characteristics. A good deal of recent attention has been focused on a subset of H-bonds that are characterized by a CH donor, rather than the more common OH or NH groups.[5−11]

One of the more interesting properties of these interactions is that the CH covalent bond tends to shorten as a result of formation of a H-bond with a Lewis base, unlike the stretching of the OH and NH bonds that is normally encountered. Associated with this contraction is a shift of the CH stretching frequency to the blue, as compared to the usual expectation of a red shift.[12−21] This interesting discrepancy has motivated a good deal of inquiry into its ultimate origin.[15,16,22−32]

Although CH···O systems exhibit a difference in IR behavior, there are quite a number of characteristics that they share with the traditional H-bonds, such as geometric preference and NMR chemical shifts.[7,33−44] The various similarities and differences have engendered a lively debate concerning the proper classification of these “blue-shifting” systems as true H-bonds, or as perhaps something different and distinct.[8,45−57]

One of the more intriguing aspects of H-bonds is their cooperativity, in the sense that a chain of *n* H-bonding molecules is held together more strongly than would be expected based on the energetics of the single H-bond within a dimer.[3,58] In other words, the whole is greater than the sum of its parts. This cooperativity is typically attributed in large measure to the polarization induced in each subunit by the presence of its H-bonding partner. Previous studies have examined the cooperativity of various sorts of H-bonded chains.[59−66] A number of recent calculations have examined this issue in the particular context of interpeptide H-bonds that may act to strengthen protein secondary structure.[67−73]

However, there has been little investigation of how CH···O H-bonds compare to their more classical OH···O or OH···N analogues in terms of cooperativity. One study[14] questioned whether multiple H-bonds act to strengthen a CH···O H-bond, as might be expected, or to weaken it, while another set of calculations found little or no effect at all.[43] Another work[74] indicated that the blue shift of a CH···O bond might be enhanced by cooperativity, but this conclusion was clouded by the simultaneous presence of stronger molecular interactions. The related CH···N types of bonds appear to show some cooperativity,[75] but there was a strong element of angular distortion that could equally be a causative factor.[76] A not entirely irrelevant CH···F type of bond does appear to undergo an enhanced blue shift as a result of cooperativity.[77]

The present work is designed to address the issue of CH···O cooperativity in a systematic and thorough manner. This sort of interaction is compared and contrasted in each respect to a chain of conventional OH···O H-bonds. In addition to the energetics of cooperativity, the calculations address the lengths of the H-bonds, including perturbations induced in the internal geometry of each monomer. Spectroscopic aspects of the interactions are considered as well, in particular the IR stretching frequencies and NMR chemical shifts of relevant nuclear centers. The work also addresses electron density shifts induced by H-bond formation, and how they are altered by the presence of multiple units in the chain. The first CH···O system considered is a chain of H_2CO molecules, varying from dimer to pentamer. The strength of these bonds is increased, without altering the basic electronic structure, by replacing one H atom of each H_2CO by the much more electronegative F atom in HFCO. These CH···O chains are contrasted with the classical OH···O bonds in water oligomers.

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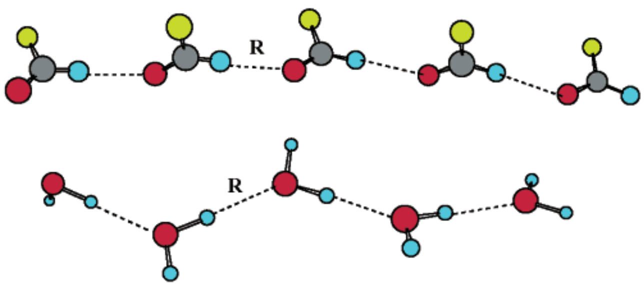

Figure 1. Geometries of pentamers considered for $(HFCO)_5$ and $(H_2O)_5$. Carbon is gray, hydrogen blue, oxygen red, and fluorine green. Shorter chains are obtained by simply removing the requisite number of molecules from either end. $(H_2CO)_5$ is similar to $(HFCO)_5$, with F atoms changed to H.

Method of Calculations

Ab initio calculations were carried out with the GAUSSIAN03 set of code, using the 6-31+G** basis set.[78] Electron correlation was included via the second-order Møller−Plessset (MP2) treatment[79,80] and the B3LYP variant of density functional theory (DFT).[81,82] NMR chemical shifts were computed by using the gauge-including atomic orbital (GIAO) approach[83] at the MP2 level, which has been shown to produce rather accurate data for hydrogen bonds.[84] The conductor polarized continuum model (CPCM)[85] using UAHF (United Atom model for Hartree−Fock/6-31G*) definition[86] for the construction of the solute cavity has been used to estimate hydrogen bond energies in different solvents at the B3LYP/6-31+G** gas-phase geometries.

Results

The geometries of the chains investigated are illustrated in Figure 1, which depicts the pentamers explicitly; shorter chains are obtained by simply removing a number of molecules from the end. Geometries were fully optimized, under the sole restriction that $\theta(XH\cdots O)$ was set equal to 180° for each H-bond. This arrangement also prevented the cyclization of some of the chains, to which they might otherwise be prone, and the associated angular distortion of the H-bonds. In the case of FCHO, $\theta(C\cdots O{=}C)$ of 135°, optimized for the dimer, was kept fixed at this value for the longer oligomers, to restrain F atoms from participating in H-bonds.

Energetics. The BSSE-corrected binding energies are grouped into one of two categories. The "end" values correspond to the energy required to break off one of the terminal molecules:

$$\Delta E_{\mathrm{end}}(n) = E(n) - [E(n-1) - E(1)] \qquad (1)$$

where $E(m)$ refers to the energy of a chain of m molecules. The breaking of the chain somewhere other than at its end is grouped into the "mid" category

$$\Delta E_{\mathrm{mid}}(n) = E(n) - [E(n-m) - E(m)] \qquad (2)$$

where $m > 1$. In the case of the tetramer, this midpoint breakage would result in a pair of dimers, while the pentamer would separate into a dimer and a trimer.

The third column of Table 1 reports a sort of "mean" H-bond energy of the entire n-mer, evaluated as the energy required to break this chain into n individual monomers, divided by $n - 1$, the number of H-bonds present.

$$\Delta E_{\mathrm{mean}}(n) = [E(n) - nE(1)]/(n-1) \qquad (3)$$

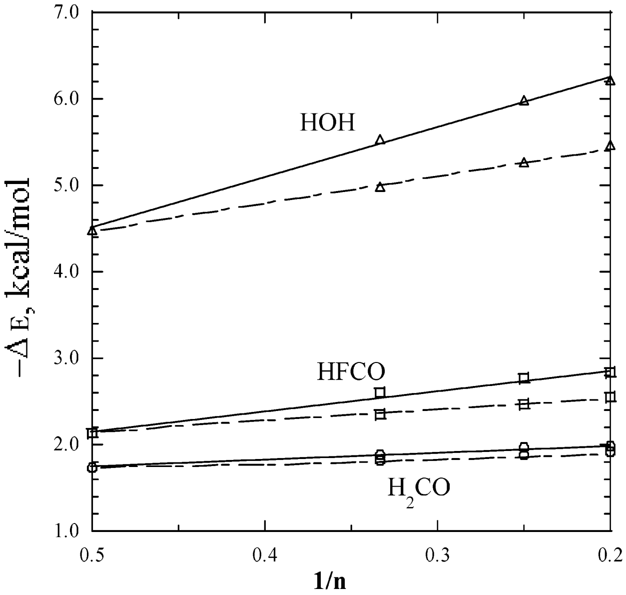

Figure 2. H-bond energies computed for chains of n monomer subunits. Solid lines represent energetics of end H-bonds; mean values derived by breaking the entire chain into monomers are indicated by broken lines.

TABLE 1: H-Bond Energies ($-\Delta E$, kcal/mol) for n-Mers of H_2CO, HFCO, and HOH

	MP2/6-31+G**			B3LYP/6-31+G** total/(n − 1)			
				$\epsilon = 1$	$\epsilon = 2$	$\epsilon = 4$	$\epsilon = 78$
n	end	mid	total/(n − 1)	vacuum	CCl_4	ether	water
				(a) H_2CO			
2	1.74		1.74	1.65	1.23	0.83	0.21
3	1.89		1.82	1.75	1.30	0.87	0.21
4	1.96	2.13	1.88	1.81	1.33	0.88	0.20
5	1.99	2.25	1.91	1.86	1.36	0.90	0.20
∞	2.17		2.02				
				(b) HFCO			
2	2.13		2.13	2.08	1.64	1.02	−0.02
3	2.60		2.35	2.32	1.77	1.11	0.02
4	2.77	3.23	2.47	2.46	1.85	1.15	0.02
5	2.83	3.46	2.55	2.55	1.90	1.18	0.03
∞	3.35		2.82				
				(c) HOH			
2	4.48		4.48	4.75	5.03	4.35	2.99
3	5.54		4.99	5.34	5.48	4.69	3.18
4	5.99	7.11	5.27	5.68	5.74	4.90	3.32
5	6.21	7.76	5.46	5.92	5.94	5.05	3.41
∞	7.43		6.09				

This quantity can be derived by pulling the complex apart, one unit at a time, from the end. In other words, $\Delta E_{\mathrm{mean}}(n)$ represents the average of the ΔE_{end} quantities for chains of length n, $n - 1$, $n - 2$, etc.:

$$\Delta E_{\mathrm{mean}}(n) = [\Delta E_{\mathrm{end}}(n) + \Delta E_{\mathrm{end}}(n-1) + \ldots + \Delta E_{\mathrm{end}}(2)]/(n-1) \qquad (4)$$

so it can also be considered as the average end binding energies of the n-mer, and all those smaller than it. The first three columns of Table 1 were all computed at the MP2/6-31+G** level.

As one might expect from cooperativity arguments, the H-bond energy increases as the chain grows longer, whether ΔE_{end} or ΔE_{mid}. The end and mean H-bond energies are depicted in Figure 2 as a function of (the reciprocal of) the length of the chain, the former by the solid lines and the latter by the broken

TABLE 2: H-Bond Lengths, R(H···O) (Å), Computed at the MP2/6-31+G Level**

	HCHO, R(C···O)			HCFO, R(C···O)			HOH, R(O···O)		
n	end, D	end, A	mid	end, D	end, A	mid	end, D	end, A	mid
2	2.4149	2.4149		2.3946	2.3946		1.9588	1.9588	
3	2.3970	2.3974		2.3057	2.2977		1.9054	1.9275	
4	2.3865	2.3934	2.3706	2.2988	2.2894	2.2661	1.8920	1.9152	1.8683
5	2.3890	2.3913	2.3666	2.2959	2.2861	2.2577	1.8856	1.9114	1.8491
∞	2.366	2.374		2.2146	2.1970		1.831	1.876	

lines. The end values are larger than the means simply because the latter averages in the values of the smaller chains, where the cooperativity is smaller.

As noted in a number of prior works,[68,74,87] H-bond energies, and certain other properties, grow very nearly linearly in relation to the reciprocal of the number of monomers in the chain. It thus becomes possible to obtain a valuable estimate of the H-bond energies when extrapolated to chains of infinite length. These values are reported in the indicated rows of Table 1. For example, the H-bond energy of the dimer of H_2CO is 1.74 kcal/mol, and grows to 2.17 kcal/mol in the infinite chain, an enhancement of 25%. These percentage increases are 57% and 66% for the HFCO and HOH chains, respectively. It would thus appear that the energetics of cooperativity, even on a percentage basis, are larger for those systems which have stronger H-bonds to begin with. The cooperativity of the HFCO chain is surprisingly large in the sense that its 57% increase is nearly as large as the 66% rise in the water chain, even though the H-bond energy of the HFCO dimer (2.13 kcal/mol) is less than half the magnitude of the 4.48 kcal/mol of the water dimer.

The measure of cooperativity mentioned above focuses on a single H-bond, say the terminal one, and monitors the change in its properties as the chain elongates. Another measure of cooperativity might focus on a given chain length, say a pentamer, and compare the properties of a terminal H-bond, wherein only one of the two participating molecules is interacting directly with others in the chain, with a H-bond occurring in the interior of the chain, in which case both of the partner molecules form H-bonds with other molecules. One may note from Table 1 that the energies of the latter type of H-bonds (labeled "mid") are consistently greater than those of the end bonds. This finding is true for CH···O and OH···O bonds alike, consistent with prior work that indicated that H-bond energies are larger within the confines of a chain of amides than on its ends.[69] Taking the pentamers as reference point, the mid H-bonds are stronger than the ends by 13%, 22%, and 25% for the H_2CO, HFCO, and HOH systems, respectively. Thus, in either means of measuring this quantity, the HFCO systems manifest a cooperativity disproportionately large, when compared with its H-bond energy.

On a final note concerning the energetics, the fourth column of Table 1 also displays the mean H-bond energy, as does the third column, and also with the 6-31+G** basis set, except that this quantity is computed with the DFT method, using the B3LYP formalism. The MP2 and B3LYP are very close indeed for the CH···O H-bonds, whereas B3LYP represents a bit of an overestimate for the water chains. However, the latter differences are small, and uniform in that the B3LYP results exhibit the same patterns as do the MP2 data in the previous column.

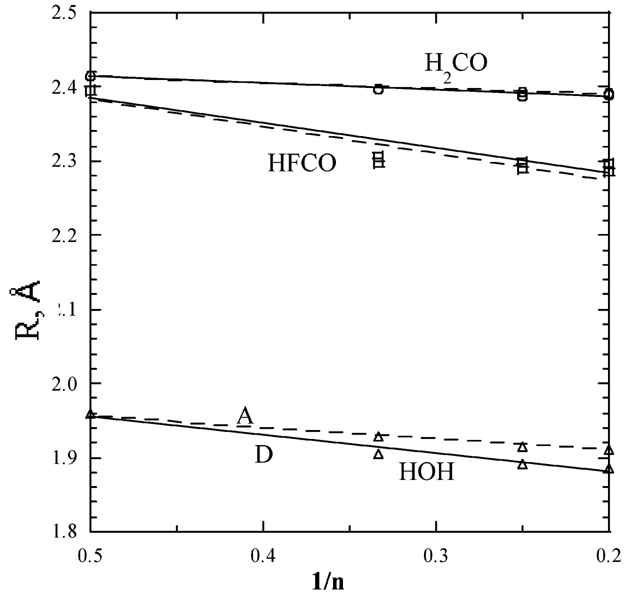

Figure 3. Lengths of end H-bonds for oligomers. Proton donor and acceptor bonds are indicated by solid and broken lines, respectively.

TABLE 3: Changes in Covalent Bond Lengths (mÅ) Relative to Monomers

	HCHO, Δr(CH)		HCFO, Δr(CH)		HOH, Δr(OH)	
n	end, D	second	end, D	second	end, D	second
2	−3.2		−1.3		5.7	
3	−3.4	−4.2	−1.2	−1.6	8.4	7.7
4	−3.4	−4.2	−1.2	−1.5	9.3	11.0
5	−3.4	−4.3	−1.2	−1.5	9.8	12.3

Geometries. The lengths of the H-bonds in the chains, reported in Table 2, fall into one of several categories. Each chain longer than $n = 2$ has two different end H-bonds, depending upon whether the terminal molecule is a proton donor (designated as D) or acceptor (A). As may be noted in Table 2, the donor end tends to be somewhat shorter than the other for HCHO and HOH, whereas the reverse is true for oligomers of HCFO. Much shorter than either of those are the H-bonds that occur in the middle of the chains, for $n > 3$. This trend is consistent with the H-bond energies in Table 1, in that the shorter middle bonds are also considerably stronger.

The terminal H-bond lengths are plotted in Figure 3 in relation to the reciprocal of the chain length. As in the case of the energies, one may note a reasonably linear correlation between these two quantities, permitting an extrapolation to infinite chain length, reported in the final row of Table 2. The percentage contractions of the D terminal H-bond lengths are 2.0%, 7.5%, and 6.5%, respectively, for the H_2CO, HFCO, and HOH chains. The HFCO would thus appear to have a perhaps anomalously large H-bond contraction, reflecting the greater slope for the HFCO curves in Figure 3.

The effects of the formation of each H-bond upon the covalent CH (or OH) bond involving the bridging proton are reported in Table 3. It is first obvious from the signs of the listed values that these bonds shorten for the CH donors, but elongate for OH. This behavior is consistent with differences that have been noted repeatedly in the literature for CH and OH donors.

Focusing first upon CH···O systems, it may be noted that the degree of bond shortening is several times greater for the HCHO chains as compared to HCFO. In either case, the bond

TABLE 4: Changes in C═O Bond Lengths (mÅ) of Proton Acceptor Molecule

	HCHO			HCFO		
n	end, A	second	third	end, A	second	third
2	1.9			2.2		
3	1.5	5.0		2.7	3.4	
4	1.5	4.7	5.2	2.7	3.8	3.5
5	1.4	4.7	5.0	2.8	3.9	4.0

contraction is larger for the second monomer in chains where $n > 2$ than for the end molecule. However, whether a terminal H-bond, or one located toward the middle of the chain, the covalent bond length is unaffected by the number of other molecules in the chain. So by this measure, the CH···O bonds display no cooperativity. The behavior of the OH bonds is quite different, in that the OH bond lengthening of the terminal HOH molecule increases quite noticeably as the chain grows longer, varying from 5.7 mÅ in the water dimer to 9.8 mÅ in the pentamer; the sensitivity to *n* is even greater for the second molecule in the chain.

From the second standpoint, that cooperativity is reflected in a greater change in the second than the first molecule, all systems demonstrate a degree of cooperativity. Taking the pentamers once again as a reference point, the increment in bond length change between the second and first molecules is a surprisingly consistent 25% for all three systems, whether CH···O or OH···O.

It is worth mentioning that it is not only the bridging XH bond lengths that are changed by formation of H-bonds; peripheral, i.e., nonbridging, bonds are affected as well. The nonbridging CH bond of the acceptor molecule of the HCHO dimer is contracted by 1.3 mÅ, relative to the isolated monomer. The analogous contraction in the HCFO dimer is 0.8 mÅ, whereas the nonbridging OH bond of the acceptor molecule in the water dimer stretches by 0.7 mÅ. That is, in all cases, the nonbridging XH bond length of the acceptor molecule changes in the same direction as the bridging XH bond, albeit to a lesser degree. Perhaps most importantly for our purposes, this quantity, the XH bond length change of the terminal acceptor molecule, is essentially unchanged as each chain grows longer, showing no evidence of cooperativity.

The proton acceptor molecule's geometry is also perturbed by the formation of a H-bond. In particular, the changes in the C═O bond length of the H_2CO and HFCO molecules are listed in Table 4. The C═O bond of the H_2CO on the acceptor end of the dimer is stretched by 1.9 mÅ; this stretch is diminished to 1.5 mÅ in the trimer, and remains at this level as the chain grows longer, indicating little cooperativity. The second, or middle, molecule in the trimer has its C═O bond stretched by much more, 5.0 mÅ, indicating the second measure of cooperativity is much higher. The behavior of the C═O bond lengths in the HFCO chains is similar in that the central molecules undergo a greater stretch than does the acceptor terminus. But there are important quantitative differences. In the first place, the C═O bond of the acceptor-end HCFO molecule elongates more than does HCHO. More importantly, this stretch is greater for longer HFCO chains, unlike the smaller stretches as the HCHO chain grows. A second important difference is that the C═O stretches of the central HCFO molecules are only slightly greater than those of the end molecule, unlike the 3-fold difference in the HCHO chains.

TABLE 5: Changes in Stretching Frequencies (cm^{-1}) of XH Bonds Involving the Bridging Hydrogen

	HCHO, $\Delta\nu$(CH)[a]		HCFO, $\Delta\nu$(CH)		HOH, $\Delta\nu$(OH)[a]	
n	end, D	second	end, D	second	end, D	second
2	37/8		26		−32/−58	-
3	38/4	51/12	26	33	−40/−107	−34/−81
4	38/3	51/8	26	32	−42/−155	−38/−112
5	38/2	52/8	26	32	−43/−121	−40/−188

[a] Asymmetric/symmetric.

TABLE 6: Changes in Chemical Shift (ppm) Involving the Bridging Hydrogen[a]

	HCHO		HFCO		HOH	
n	end, D	second	end, D	second	end, D	second
2	−0.5/0.3		0.8/9.2		−2.8/10.6	
3	−0.5/2.1	−0.8/1.9	0.7/9.6	0.6/9.7	−3.5/12.2	−3.6/11.5
4	−0.5/2.1	−0.8/2.1	0.7/9.8	0.5/10.2	−3.7/12.7	−4.4/13.4
5	−0.6/2.1	−0.8/2.1	0.7/9.8	0.5/10.4	−3.8/13.0	−4.7/14.1

[a] Isotropic/anisotropic.

Vibrational Spectra. It is normally observed that the bridging OH bond elongations of conventional OH···X H-bonds are accompanied by a red shift of the associated OH stretching frequency. Recent research has revealed an analogous relationship between contractions of CH bonds and blue shifts of the CH vibrational band. This pattern holds in the investigated oligomers as well, as indicated by comparison of Tables 3 and 5, the latter of which reports the calculated changes in the pertinent CH and OH stretching frequencies, again relative to the monomers. In the cases of both H_2CO and H_2O, there are of course two hydrogens on each molecule, so one cannot unambiguously associate a single stretching frequency with one particular CH or OH bond. The table thus lists both the asymmetric and symmetric stretching frequency changes; nevertheless, the patterns are clear.

The CH stretching frequencies of H_2CO and HCFO shift to the blue, while the OH band of HOH shifts to the red. The perturbations of the end molecule are unaffected by the number of molecules in the chain, as was noted in Table 3 for the CH bond lengths. Another commonality is the smaller set of changes within HCFO than in H_2CO (at least with respect to the asymmetric stretches of the latter). The red OH shifts within the HOH molecule are quite large, and continue to climb as the chain of water molecules elongates, in a clear manifestation of cooperativity.

Our alternate measure of cooperativity, on the other hand, indicates an opposite result, of *lesser* cooperativity for the OH than for the CH bonds. That is, whereas the second molecule from the donor end of the CH···O chains undergoes a substantially greater change in frequency than does the first, the opposite is true for the H_2O chains where the interior molecule suffers a smaller red shift. In that sense, the behavior of the stretching frequencies in the water chains is opposite to that observed in the OH bond lengths of Table 3.

NMR Chemical Shift. Another key indicator of hydrogen bonding is the change in the NMR chemical shift of the bridging hydrogen that results from the formation of the interaction. These shifts are reported in Table 6, relative to the isolated monomer, and reveal some interesting patterns. Focusing first on the isotropic shifts, these quantities are negative for both H_2CO and H_2O, but positive for HFCO. In the case of the two CH donors, there is little sensitivity to the number of H-bonds in the chain, whereas a steady increase in the magnitude is observed for HOH chains, indicating cooperativity. The second aspect of cooperativity, a larger effect for interior than for terminal molecules, is present for H_2CO and H_2O, but absent in HFCO.

The anisotropic shifts are positive for all three types of system. Values are largest for the conventional OH···O bonds of the

TABLE 7: Changes in Chemical Shift (ppm) of the Proton-Accepting O Atom[a]

	HCHO		HFCO		HOH	
n	end, D	second	end, D	second	end, D	second
2	0.8/−6.3		3.6/−5.4		−2.6/−2.6	
3	2.6/−0.9	5.7/−11.3	5.8/−5.2	4.6/−6.3	−6.3/3.1	−1.9/−1.5
4	2.4/−1.0	3.2/−4.3	6.4/−5.9	6.9/−6.4	−7.9/4.5	−6.3/4.9
5	2.5/−1.4	3.0/−4.5	6.6/−6.1	7.5/−7.1	−8.4/5.1	−8.1/6.4

[a] Isotropic/anisotropic.

water chains, in the range of 11−14 ppm. This range compares with some 10 ppm for the HFCO chains and 2 ppm for H_2CO. The anisotropic shifts of the latter group of systems, containing the weakest H-bonds, are not affected by either the number of units in the chain or the placement of the H-bond along the chain (first or second). In the case of the HFCO chains, the second H-bonds have a slightly larger anisotropic shift than do the first, and the values increase as the chain elongates. These same trends are present in the HOH chains, but to a much larger extent.

The chemical shifts of the proton-accepting O atoms are very different from one system to the next, as evident in Table 7. The isotropic shifts of the terminal H_2CO molecules are displaced downfield by 1−3 ppm, those for HFCO increase by 4−7 ppm, while those of the HOH molecules move in the opposite direction, as illustrated graphically in Figure 4. For the H_2CO systems, there is an increase on lengthening the chain from dimer to trimer, but none beyond that. The fluorinated HFCO oligomers display a continuing increase even up to the pentamer level, as do the water chains. The penultimate molecule undergoes a much larger change in O isotropic shift in the H_2CO systems, a difference that moderates with chain elongation; indeed, the shift of this second molecule diminishes as H_2CO molecules are added to the chain. In contrast, the penultimate O atom of the HFCO chains manifests a rapid rise in isotropic shift, steeper than that of the terminal molecule. A similar trend is observed for the water chains, albeit upfield instead of downfield.

All of the O anisotropic shifts are negative for the CH···O bonded chains, while the sign is variable for $(HOH)_n$. Whereas the magnitude of this change is relatively uniform for all of the HFCO chains (5−7 ppm), it is quite sensitive to chain length and to monomer position in $(H_2CO)_n$, varying between 1 and 11 ppm. In the H_2CO trimer, for example, there is a difference of 10 ppm between the values for the end molecule and its immediate neighbor. Strong sensitivity to the number of subunits is noted in the HOH chains as well, including a reversal in sign. The water oligomers obey a pattern wherein the O anisotropic shift becomes progressively more positive as the chain grows longer, just as the isotropic shift becomes more and more negative, a sign of cooperativity.

Electron Density Shifts. It is well recognized that the bridging proton loses electron density, i.e., becomes more positively charged, as the result of H-bond formation. Table 8 indicates this trend is characteristic of all H-bonds studied here, CH···O as well as OH···O. In fact, the magnitudes of these changes are not very different from one system to the next. All oligomers display some cooperativity, with charge increases rising as the chain elongates, and in all cases, the second molecule from the donor end undergoes a larger change than does the terminal molecule.

Along with the increased positive charge of the bridging hydrogen, there is typically a transfer of net charge that occurs between the donor and acceptor molecules upon formation of a H-bond. The electron density flows from the proton acceptor molecule to the donor, causing a greater negative charge on the latter and more positive charge on the former. These trends are repeated for the H-bonded chains as well, as evident by the charge changes listed in Table 9 for the molecules on both ends of each chain. The changes are somewhat smaller for the CH···O bonds in the HCHO and HFCO chains, as compared to the water oligomers. Whereas the amount of charge flow increases with chain length in the HOH systems, there is very little such growth in the CH···O bonds beyond the trimer level.

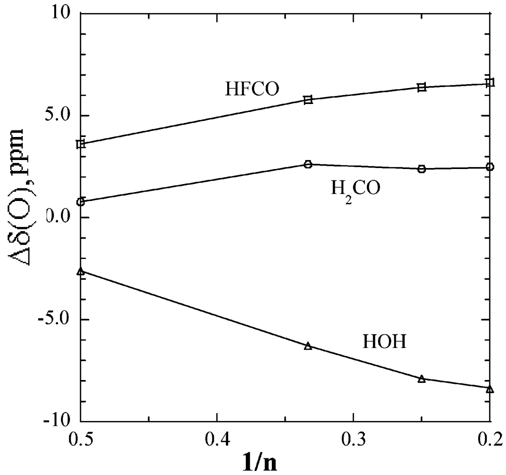

Figure 4. Displacements, relative to isolated monomers, of isotropic chemical shifts of the proton-accepting O atom of the terminal molecule in chains of *n* subunits.

TABLE 8: Changes in Natural Population Atomic Charge (me) of the Bridging Hydrogen

	HCHO		HFCO		HOH	
n	end, D	second	end, D	second	end, D	second
2	16		18		19	
3	19	25	20	24	24	33
4	21	27	21	27	25	38
5	22	28	21	28	23	36

TABLE 9: Changes in Natural Population Group Charge (me) Undergone by Terminal Molecules

	HCHO		HFCO		HOH	
n	D	A	D	A	D	A
2	−8.6	8.6	−8.4	8.4	−13	13
3	−9.3	8.4	−9.5	10.0	−18	17
4	−9.6	8.2	−9.7	10.3	−19	18
5	−9.4	8.0	−9.8	10.0	−21	19

Effect of Surroundings. Of course most H-bonds do not occur within a vacuum, isolated from other species. It is thus important to consider how these interactions, and in particular their cooperativity, is affected by their surroundings. The various H-bonded chains were therefore immersed in various solvents, each represented by a continuum with the dielectric constant ϵ characteristic of that solvent. The right side of Table 1 reports the average H-bond energy (again, computed as the energy required to break the *n*-mer apart into *n* separate monomers, divided by the number of H-bonds in the chain) for dielectric constants varying from unity (vacuum) to 2 for CCl_4, up to 78 to represent aqueous solution.

Scanning the data from left to right indicates the H-bonds generally weaken as the dielectric constant increases. This pattern is consistent with the idea that separated monomers are more stabilized by interaction with a dielectric continuum than are the H-bonded chains. (There is an interesting exception to this rule for the water chains, which are more tightly bound for $\epsilon = 2$ than in a vacuum, but the H-bonds then weaken as ϵ progresses to higher values.) Placement in solvent retains the general principle of cooperativity, in the sense that the H-bonds strengthen as each chain grows longer.

However, there is a clear lessening of the cooperative effect as the solvent becomes more polar. Taking the HCHO chains as an example, the mean H-bond energy in the pentamer is greater than that in the dimer by 0.21 kcal/mol in vacuo, whereas this difference diminishes to 0.13 in CCl_4, 0.07 for $\epsilon = 4$, and vanishes entirely in water. A similar reduction in cooperativity is observed in the other CH···O bonded chains involving HFCO. Where the water chains differ is that they retain their energetic cooperativity, even when ϵ has climbed to 78. Even at this high value of ϵ, the mean H-bond energy of the water pentamer is 14% higher than that in the monomer.

Summary and Discussion

As expected, the HFCO monomers are bound together by stronger CH···O H-bonds than are the unfluorinated H_2CO units; the conventional OH···O H-bonds in water chains are in turn stronger than both. Stronger H-bonds also tend to be shorter, and induce greater perturbations in the geometries of the subunits, as well as to their IR and NMR spectra. The chief focus of this work, however, lies in the cooperativity that makes each H-bond within a chain different than any single H-bond connecting two monomers. Two measures are used here to assess cooperativity. The first considers a particular H-bond, the terminal one, and monitors its properties as the chain grows longer. The second metric compares a terminal H-bond with one more centrally located in the chain, which is surrounded by molecules on both sides.

In a number of respects the CH···O H-bond mirrors the cooperativity of the more conventional H-bonds, although there are some significant differences as well. Either sort of interaction grows stronger as the number of monomers in the chain increases. The degree of cooperativity is roughly proportional to the strength of the H-bond. Thus, one sees a sharper growth of H-bond strength accompanying chain elongation in the order $(H_2CO)_n < (HFCO)_n < (H_2O)_n$. The H-bond energies obey a very nearly linear relationship with the reciprocal of the number of bonds, permitting extrapolation to much longer chains. It is thus estimated that the mean H-bond energy in an infinite chain of H_2CO molecules is 25% greater than the same quantity in a dimer, while the long water chain exhibits a 66% enhancement over $(H_2O)_2$. Although containing substantially weaker individual H-bonds than those in water chains, $(HFCO)_n$ manifests an energetic cooperativity that is nearly as large as that of the OH···O congeners. Likewise, a projection of H-bond lengths to infinite chains confirms a surprisingly high degree of cooperativity in $(HFCO)_n$, in this case even greater than that noted in OH···O chains. H-bonds that occur in the interiors of each chain are stronger, and shorter, than terminal H-bonds. The magnification in strength, within the context of the pentamer, is 13%, 22%, and 25% for the H_2CO, HFCO, and HOH systems, respectively, another indication that the cooperativity is directly related to intrinsic H-bond energy, and that in $(HFCO)_n$ is disproportionately large.

Consistent with a number of prior works, it is found here that the CH covalent bond of both H_2CO and HCFO shortens when engaged in a CH···O interaction, while the analogous OH bond of water is stretched. The degree of bond contraction is considerably smaller for the HFCO chains than for their H_2CO analogues, even though the corresponding H-bonds of the former are stronger. Even more interesting, the CH bond contractions show no evidence of cooperativity, whereas the OH bond stretches of $(H_2O)_n$ continue to grow as n increases. Comparable patterns are observed in the stretching frequencies of the CH and OH bonds. The blue shifts that accompany CH···O bond formation are greater for $(H_2CO)_n$ than for $(HFCO)_n$, and these shifts are unaffected by chain length. In contrast, the OH shifts of $(H_2O)_n$ are to lower frequency, and become more pronounced as the water chain becomes longer.

From the alternate perspective of assessing cooperativity, a comparison of internal vs terminal H-bonds, all three systems exhibit a nearly constant level of cooperativity. That is, the CH (or OH) bond length changes in the interior H-bonds are 25% greater for the second H-bond than for the first. A similar analysis of vibrational frequency changes suggests that the CH blue shifts are *more* cooperative than are the red shifts in the OH frequencies.

Formation of the H-bonds perturbs the NMR chemical shift of the bridging proton. The isotropic and anisotropic perturbations are negative and positive, respectively, for the classical OH···O bonds. These alterations are similar in sign, albeit smaller in magnitude, for the CH···O bonds of $(H_2CO)_n$. The anisotropic shifts in the HFCO oligomers are much larger, comparable to those in $(H_2O)_n$; the isotropic shifts become more positive, contrasting with their negative signs for both $(H_2CO)_n$ and $(H_2O)_n$. As was the case for XH stretching frequencies, the cooperativity in evidence with growing n for the OH NMR chemical shifts disappears when considering CH bonds; the latter CH bonds manifest reduced cooperativity by the second measure as well, comparing interior with terminal H-bonds.

The chemical shift of the proton-accepting O atom is equally interesting. The isotropic quantity is quite negative for $(H_2O)_n$, and increases rapidly with elongating chain. The isotropic shift of the carbonyl O of $(HFCO)_n$ is of opposite sign, but also shows signs of cooperativity. This same quantity is also positive for $(H_2CO)_n$ but shows little evidence of dependence upon chain length (beyond $n = 2$). Anisotropic shifts are similar in the sense that this quantity appears to be cooperative in both $(H_2O)_n$ and $(HFCO)_n$ (although the signs differ in these two systems), but sensitivity to n is weaker in $(H_2CO)_n$.

Patterns in charge shift are consistent with many of the trends noted above. All bridging protons, whether OH···O or CH···O, become more positive upon forming a H-bond. This change is larger for the stronger OH···O; all systems show signs of cooperativity as n increases, or as the second H-bond is compared to the first. There is also a certain amount of electron density that transfers from the proton acceptor molecule to the donor. Again, these group charge transfers are larger for the water oligomers, with their OH···O H-bonds. There is some evidence of cooperativity for the stronger OH···O systems, less for CH···O.

Placement of the chains in the context of a dielectric continuum indicates a weakening H-bond, as well as a diminishing degree of cooperativity, with growing dielectric constant. All evidence of cooperativity vanishes for the CH···O chains when ϵ reaches 78, whereas the OH···O H-bonds strengthen with greater n even at this high value of ϵ.

One might wonder how the results described herein might have been affected by the use of a different basis set. There have been a number of published sets of calculations that addressed the issue of the sensitivity of H-bond cooperativity to basis set.[3,88] There is by and large a consensus that this sensitivity is surprisingly low. For example, an early study of HCN polymers[89] indicated that the percentage rise in H-bond energy, upon going from dimer to an infinite chain, remained in the 40−44% range when the basis set was expanded from minimal STO-3G to [5,3/3] and then to [641/41] including polarization functions. In the case of water molecules, a similar enlargement from dimer to infinite chain yielded a 45−53% enhancement, again rather insensitive to basis set choice, ranging from DZ to highly polarized TZ(3d2f,3p2d).[90] The contraction of the H-bond lengths manifested similar insensitivity, remaining in the 0.14−0.16 Å range for all. HF and HCl polymers have also been considered. H-bond energy increments upon going from $(HF)_2$ to $(HF)_{10}$ lie in the narrow range of 85−89% for aug-cc-pVDZ, VTZ, and VQZ.[91] An analogous lack of sensitivity to basis set choice was observed for three-center H-bonds as well, wherein both 6-31+G* and 6-311++G(2d,2p) basis sets (at the MP2 level) show an identical rise in H-bond energy upon going from diformamide dimer to pentamer.[74] It is thus reasonable to conclude that the data contained in this report are unlikely to be much affected by a larger basis set.

Acknowledgment. This work was supported by NIH grant GM57936.

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