Hydrogen Bonding to Alkanes: Computational Evidence

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The structural, vibrational, and energetic properties of adducts of alkanes and strong cationic proton donors were studied with composite ab initio calculations. Hydrogen bonding in D−H$^+$···H−alkyl adducts contributes to a significant degree to the interactions between the two components, which is substantiated by NBO and AIM results. The hydrogen bonds manifest themselves in the same manner as conventional hydrogen bonds, D−H bond elongation, D−H vibrational stretching frequency red shift and intensity increase, and adduct stabilization. The alkane adducts also exhibit elongation of the C−H bonds involved and a concurrent red shift, which is rationalized in terms of charge-transfer interactions that cause simultaneous weakening of both the O−H and C−H bonds. Like other dihydrogen-bonded adducts, the adducts possess a bent structure and asymmetric bifurcated hydrogen bonds. The hydrogen bonds are stronger in adducts of isobutane and in adducts of stronger acids. Intramolecular hydrogen bonding in protonated long-chain alcohols manifests itself in the same manner as intermolecular hydrogen bonding and can be equally strong.

Introduction

According to Pauling, the conventional hydrogen bond "...is formed only between the most electronegative atoms";[1] it is of the form D−H···A, where D is an electronegative atom such as O or N and both D and A have at least one lone pair.[2] In the view generally adopted today, hydrogen bonding encompasses a greater variety of donors and acceptors, for example, any electron-rich region such as π-bonds[3] and alkyl radicals[4] can be a hydrogen bond acceptor.

Despite the diversity, hydrogen bonding can nearly always be described as an incipient proton transfer.[5−7] This suggests that all molecules capable of participating in Brønsted acid−base reactions may also form hydrogen bonds and prompted us to take a closer look at a group of weakly basic molecules, alkanes.

The protonation of alkanes by superacids has been investigated extensively theoretically and experimentally,[8] but that alkanes could be hydrogen bond acceptors was not described in these studies. However, Ahlberg[9] suggests hydrogen bonding in adducts of methane and $H_3F_2^+$; the interaction between methane and the more acidic H_2F^+ results in proton transfer. Kryachko and Zeegers-Huyskens[10] found that an adduct of methane and the protonated water dimer exhibits what they call multidihydrogen bonding; the formation of gas-phase adducts of methane and protonated water was observed by Field and Beggs[11] and by Cao, Sun, and Holmes.[12] Legon et al.[13] obtained microwave spectra of hydrogen-bonded adducts of methane and various donors.

The characteristic properties of hydrogen-bonded adducts are D−H bond elongation, red shift of the accompanying vibrational stretching frequency with attendant increase in infrared intensity, and stabilization relative to the isolated components.[2,6] These properties can conveniently be examined computationally, which facilitates studies of the intra- and intermolecular interactions between alkanes and strong organic proton donors; in the present study, we examine the adducts between protonated alcohols, aldehydes, carboxylic acids, and water as donors and methane, ethane, propane, and isobutane as acceptors. The study also includes the intramolecular interactions in protonated long-chain alcohols. The proton affinities (PA) of the donors span more than 100 kJ mol^{-1}, but none of the proton donors are strong enough to protonate the alkane.

Computational Methods

Structure and harmonic vibrational frequencies of molecules and hydrogen-bonded adducts were determined with the B3LYP/6-31+G(d,p) method. The G3//B3LYP and G3(MP2)//B3LYP composite ab initio methods[14] were used to estimate the thermochemical properties of the species studied; the 298 K heats of formation were obtained as described by Nicolaides et al.[15] All calculations were performed with the Gaussian 03 package.[16]

Strong coupling of the O−H and C−H stretching vibrations to other modes was often encountered; in order to determine the red shifts of the harmonic stretching frequencies, we have, where appropriate, employed "virtual isotope labeling" to assess the vibrational properties in the absence of coupling. This technique, also used by others,[17] involves calculation of the vibrational properties of suitably deuterium-substituted analogues in order to avoid coupling to the vibration of interest.

The stabilization of the hydrogen-bonded adducts was calculated as the difference between the heats of formation of the adduct and the isolated components and takes into account the bonding between the adduct components as well as the deformation of these components that accompanies adduct formation. It is possible to estimate the deformation energy of each component as the difference between the energy of that component in isolation and with the adduct structure, and hence to account explicitly for the deformation. However, we choose to express the adduct stabilization as the negative of the enthalpy of association, which brings it in line with conventional definitions of bond strength. Proton affinities were calculated as the difference between the G3//B3LYP energies of the neutral and the protonated molecule, adding 5/2RT, 6.2 kJ mol^{-1}.

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TABLE 1: Structural, Vibrational, and Energetic Properties of Adducts of Alkanes and H_3O^+ or $CH_3CH_2OH_2^+$

	Δr_{OH}[b]	$\Delta \upsilon_{OH}$[b]	Δr_{CH}[b]	$\Delta \upsilon_{CH}$[b]	E_{stab}[c]
			H_3O^+		
methane[a]	0.039	743	0.008, 0.009	74, 92	34 [3]
ethane[a]	0.045	841	0.014, 0.014	110, 122	42 [4]
propane[a]	0.053	965	0.009, 0.019	103, 199	47 [5]
isobutane	0.059	1024	0.038	369	51 [6]
			$CH_3CH_2OH_2^+$		
methane[a]	0.018	356	0.006, 0.007	57, 72	22 [3]
ethane[a]	0.021	427	0.008, 0.010	78, 113	29 [3]
propane[a]	0.025	494	0.009, 0.013	102, 153	33 [4]
isobutane	0.026	516	0.024	247	35 [5]

[a] Two C−H bonds involved. [b] Changes with respect to the non-hydrogen-bonding O−H bond, where appropriate; otherwise, the changes are with respect to the isolated component; Å, cm^{-1}; B3LYP/6-31+G(d,p). [c] The stabilization calculated as the difference between the heats of formation of the adduct and the isolated components; kJ mol^{-1}; G3//B3LYP; counterpoise correction in brackets.

The results are not corrected for basis set superposition error (BSSE) as it is unclear how this would be taken into account for adducts that may be partially covalently bonded.[18] The counterpoise corrections[19,20] to the G3//B3LYP results are shown in parentheses in the tables; they are obtained for each of the component calculations and summed in the same manner as the electronic energies in a G3-type calculation.[21] The corrections are in the range of 2−6 kJ mol^{-1}, that is, around 10% of the stabilization.

The AIM[22] and NBO[23] methods were employed to further investigate the properties of the hydrogen-bonded adducts. These calculations were performed with the facilities available in Gaussian 03. As an aid to the interpretation, we have made use of the Molden and Xaim programs.[24]

Intermolecular Hydrogen Bonds

The presence of intermolecular hydrogen bonds from strong, ionic acids to alkanes is made apparent by the indicators of conventional hydrogen bonding, O−H bond length change, IR red shift, and stabilization.[2,7] In addition, the structure of the acceptor alkane also changes; the C−H bonds involved are elongated considerably, which is unusual as the acceptor in conventional hydrogen-bonded adducts in most cases undergoes very little structural change. Correspondingly, the vibrational stretching frequencies of the C−H bonds are also red shifted, and the infrared intensity increases upon adduct formation.

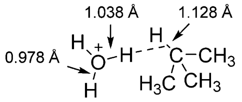

Figure 1. Adduct of protonated water and isobutane (B3LYP/6-31+G(d,p)).

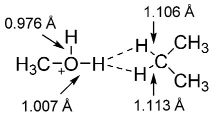

Figure 2. Adduct of protonated methanol and propane (B3LYP/6-31+G(d,p)).

Structural and Vibrational Properties. The elongation of the O−H and C−H bonds that accompanies formation of hydrogen-bonded alkane adducts is illustrated in Tables 1 and 2. The O−H bond length increases by up to 6%, the C−H bond lengths by up to 3%. The structural changes are correlated to the hydrogen bond strength, larger changes correspond to stronger hydrogen bonding; in the present systems, the strongest hydrogen bond is formed in the adduct of protonated water and isobutane, Figure 1.

The stronger hydrogen bonds in adducts of propane involve the CH_2 group, in which both C−H bonds are involved in the hydrogen bonding, as illustrated in Figure 2. Similar bifurcated hydrogen bonds were described by Zeegers-Huyskens for the $H_5O_2^+$−methane adduct;[10] it appears that two carbon-bonded hydrogens are involved whenever CH_2 or CH_3 groups engage in hydrogen bonding, Table 1. However, the two C−H bonds are not elongated to the same extent, indicating unequal interaction with the proton donor. Both Ahlberg[9] and Zeegers-Huyskens[10] observe this asymmetry in hydrogen-bonded methane adducts in which the two C−H bonds involved are not equally long. The C−H bond length changes follow the O−H bond length change in the donor, which illustrates that the strength of alkane dihydrogen bonding is reflected in the length of all bonds involved. The C−H bond length changes are noticeably larger in adducts of isobutane than in adducts of the other alkanes, possibly because only one C−H bond participates in the hydrogen bond.

The results in Table 2 show that the donors with lower proton affinities (the stronger acids) form the stronger hydrogen bonds to alkanes; however, the adducts of protonated carboxylic acids exhibit slightly smaller structural changes than their proton affinities would suggest.

The distance between the interacting hydrogen atoms is between 1.3 and 2.0 Å, consistently smaller than the sum of

TABLE 2: Structural, Vibrational, and Energetic Properties of Adducts of Isobutane and Strong Organic Proton Donors

donors (PA)[a]	Δr_{OH}[b]	$\Delta \upsilon_{OH}$[b]	I_{OH}[c]	Δr_{CH}[b]	$\Delta \upsilon_{CH}$[b]	I_{CH}[c]	r_{HH}[d]	ε, ζ, Ψ[e]	E_{stab}[f]
H_3O^+ (689)	0.059	1024	5	0.038	396	9	1.298	119, 170, 129	51 [6]
$HC(OH)_2^+$ (743)[g]	0.022	515	9	0.022	221	5	1.449	125, 162, 143	38 [5]
$CH_3OH_2^+$ (755)	0.032	644	7	0.028	284	6	1.425	121, 170, 131	40 [5]
CH_3CHOH^+ (772)	0.028	569	8	0.029	303	7	1.438	119, 170, 129	36 [6]
$CH_3CH_2OH_2^+$ (778)	0.026	516	12	0.024	247	5	1.476	122, 171, 131	35 [5]
$CH_3C(OH)_2^+$ (788)[g]	0.018	404	8	0.025	260	7	1.501	126, 174, 131	33 [6]
$(CH_3)_2OH^+$ (793)	0.022	465	8	0.025	260	6	1.485	121, 172, 129	37 [6]
$H_2O \cdot H_3O^+$ (815)	0.019	408	7	0.021	232	7	1.535	123, 171, 132	25 [5]

[a] Proton affinities of the corresponding neutral donors; kJ mol^{-1}; G3//B3LYP. [b] Changes with respect to the non-hydrogen-bonded O−H bond, where possible; otherwise, changes are with respect to the isolated component; Å, cm^{-1}; B3LYP/6-31+G(d,p). [c] Factor of infrared intensity increase with respect to the non-hydrogen-bonded O−H bond, where appropriate; otherwise, it is with respect to the isolated component; B3LYP/6-31+G(d,p). [d] Distance between donor and acceptor hydrogen; Å. [e] ε, ζ, and Ψ are the angles in Figure 3; degrees; B3LYP/6-31+G(d,p). [f] The stabilization calculated as the difference between heats of formation between the adduct and the isolated components; kJ mol^{-1}; G3//B3LYP; counterpoise correction in brackets. [g] The *E*,*Z* conformer; adduct formed via the *E* OH group.

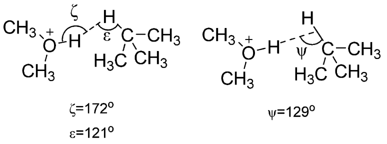

Figure 3. Adduct of isobutane and protonated dimethyl ether (B3LYP/6-31+G(d,p)).

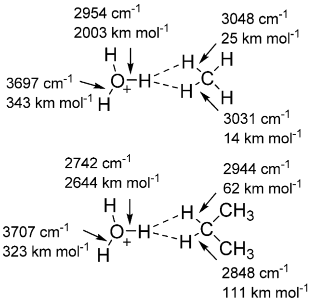

Figure 4. Harmonic stretching frequencies and IR intensity of the adducts of protonated water and methane and propane (B3LYP/6-31+G(d,p)).

the van der Waals radii of two hydrogen atoms (Table 2). The proximity of the hydrogen atoms further substantiates that the alkane adducts are not merely van der Waals adducts, but that the bonding is partially covalent.

The O−H and C−H bonds are not linearly aligned; rather, the O−H bond "points" to the middle of the C−H bond, as illustrated in Figure 3. The result is a bent structure, conspicuously different from the linearity observed for conventional hydrogen bonds. The structures of adducts calculated with MP2 methods are in general quite similar to those determined with B3LYP calculations, except that the relative orientation of the donor and acceptor is different in the case of methane, for example. The donor hydrogen in the protonated water adduct is equally close to three of the methane hydrogens when determined with MP2(full)/aug-cc-pVTZ calculations; the structure of that adduct is similar to that of the neutral adduct of water and methane.[25]

Typical O−H and C−H stretching frequencies and infrared intensity increases are shown in Figure 4; other values are in Table 1 and 2.

The vibrational changes are a very sensitive measure of the hydrogen bond strength, perhaps too sensitive; the red shift is a direct consequence of the bond length changes.[26] The red shift and the bond length change therefore exhibit similar trends.

AIM and NBO. Examination of the alkane adducts with the AIM method[22] confirms that it is appropriate to describe the interaction between strong proton donors and alkanes as hydrogen bonding. Koch and Popelier[27] suggested that the value of the Laplacian of the electron density at the bond critical point will be between 0.024 and 0.139 au for most hydrogen bonds. For the adducts studied here, the values of the Laplacian of the electron density at the bond critical point of the H···H hydrogen bond lie within this range, as exemplified in Table 3 for the adducts of isobutane.

The covalent contribution to the hydrogen bond can be examined with the NBO method,[23] which facilitates assignment of the interactions that give rise to the charge-transfer contribution to the bonding. Our results show that the main charge-transfer contribution derives from interaction of the O−H σ^*-orbital of the donor with the σ-orbital(s) of the C−H bond(s) of the alkane and that the occupancy of these orbitals is correlated to the bond length changes and adduct stabilization (Tables 2 and 3).

TABLE 3: AIM Electron Density (ρ) and Laplacian (∇^2) at the Bond Critical Point of the H···H Hydrogen Bond and the NBO Occupation of the O−H σ^*- and C−H σ-Orbitals in Adducts of Isobutane and Strong Organic Proton Donors[a]

donors (PA[b])	ρ	∇^2	occ. σ_{OH}*	occ. σ_{CH}
H_3O^+ (689)	0.053	0.042	0.100	1.891
$HC(OH)_2^+$ (743)[c]	0.032	0.053	0.057	1.933
$CH_3OH_2^+$ (755)	0.037	0.059	0.067	1.923
CH_3CHOH^+ (772)	0.037	0.054	0.063	1.929
$CH_3CH_2OH_2^+$ (778)	0.033	0.054	0.055	1.933
$CH_3C(OH)_2^+$ (788)[c]	0.030	0.051	0.054	1.937
$(CH_3)_2OH^+$ (793)	0.032	0.054	0.058	1.933
$H_2O\cdot H_3O^+$ (815)	0.027	0.053	0.042	1.943

[a] AIM density in atomic units; NBO occupation in e. [b] Proton affinities of the corresponding neutral donors; kJ mol^{-1}. [c] The *E*, *Z* conformer; adduct formed via the *E* OH group.

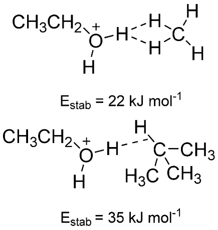

Figure 5. Stabilization of adducts of protonated ethanol and methane and isobutane (B3LYP/6-31+G(d,p)).

Adduct Stabilization. Formation of adducts of strong, ionic proton donors and alkanes is accompanied by stabilization, and although this stabilization does not accurately reflect the hydrogen bond strength, it does provide a means to compare hydrogen bonds in a homologous group of hydrogen-bonded adducts. This allows us to take the hydrogen bond to be stronger in the adduct of protonated ethanol and isobutane than in the adduct of protonated ethanol and methane, Figure 5, in good agreement with the bond length and IR changes, Table 1. Correspondingly, the adduct stabilization is larger in the adducts with the stronger hydrogen bond, that is, in the adducts of isobutane and of the stronger acids (Tables 1 and 2).

The formation of hydrogen bonds only accounts for part of the adduct stabilization. The latter arises to a considerable extent from ionic interactions, that is, from the electrostatic multipole interactions that necessarily exist between ions and polarizable neutrals; these interactions are distinct from the local electrostatic interactions that are part of the hydrogen bonding.[7]

The deformation influences the adduct stabilization because the molecules are distorted from their equilibrium structure as a consequence of adduct formation. The energy required to distort the components diminishes the stabilization and hence the apparent hydrogen bond strength. It can be calculated for each component as the difference between the energy of the isolated component and that of the same component with the adduct structure. The components of the stronger bonded adducts undergo the larger structural changes and therefore also exhibit larger deformation energies. The acceptor C−H bonds contribute more to the total energy of deformation than does the O−H bond. For the adduct of protonated water and isobutane, the deformation energy of H_3O^+ is 4.9 kJ mol^{-1}, and 6.5 kJ mol^{-1} for C_4H_{10}.

The adduct stabilization can roughly be expressed in terms of these contributions

$$E_{\text{stab}} = E_{\text{ion}} + E_{\text{HB}} - E_{\text{def}} \qquad (1)$$

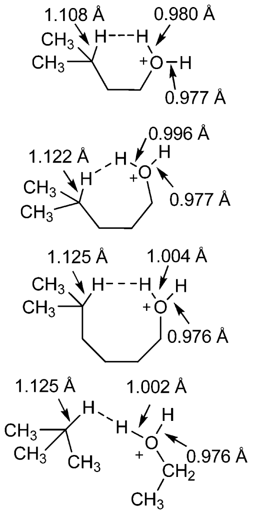

Figure 6. Hydrogen-bonded conformers of protonated 3-methyl-1-butanol, 4-methyl-1-pentanol, 5-methyl-1-hexanol, and, for comparison, the adduct of isobutane and protonated ethanol (B3LYP/6-31+G(d,p)).

where E_{ion} is the stabilization due to ionic interactions, E_{HB} the stabilization due to hydrogen bonding, and E_{def} the deformation energy. Unfortunately, these three quantities are not independent, and they can only be estimated relatively crudely. In particular, the energetic consequences of the ionic interactions and the hydrogen bonding cannot be determined separately, but the former probably accounts for the lion's share in the present systems. It has been observed previously that ionic interactions in general influence the stabilization of charged adducts to such an extent that it is not a particularly good measure of the strength of hydrogen bonds.[28]

Intramolecular Hydrogen Bonding to Alkyl Groups

Long-chain protonated alcohols exhibit hydrogen bonding to remote alkyl groups within the molecule (Figure 6). Protonated 5-methyl-1-hexanol, for example, forms an eight-membered ring with an intramolecular hydrogen bond; the changes of O−H and C−H bond lengths and vibrational properties are not very different from those in the intermolecular adducts.

Using the bond length changes and IR red shift to assess the hydrogen bond strength, Figure 6 illustrates that the hydrogen bond is weaker in the smaller rings, indicating that the structural restrictions can make hydrogen bond formation less favorable. The interaction in protonated 3-methyl-1-butanol gives rise to an O−H bond length change of only 0.002 Å, which suggests that the hydrogen bond is very weak, if there at all. Corroboration is provided by NBO studies that show no evidence of charge-transfer interactions that involve six-membered rings; however, our NBO and AIM results substantiate that the intramolecular hydrogen bonds in the larger rings are closely related to those in the bimolecular adducts.

The hydrogen bond in the eight-membered ring of protonated 5-methyl-1-hexanol is as strong as that in the adduct of isobutane and protonated ethanol, judged by the bond length changes and red shifts. The stabilization indicated in Table 4 does not appear to reflect this because unfavorable gauche interactions detract from the overall stabilization of the cyclic systems. The marginal stabilization of the internally hydrogen-bonded protonated pentanol does not signify that hydrogen bonding is absent but rather that the effect of hydrogen bond stabilization and gauche interactions cancel. The intramolecular interactions between O−H bonds and tertiary C−H bonds are stronger than those involving CH_2 and CH_3 groups. The calculated OH stretching vibrational frequencies of protonated 1-pentanol, 1-hexanol, and 5-methyl-1-hexanol (all eight-membered ring hydrogen bonds) illustrate this trend, exhibiting red shifts of 384, 483, and 555 cm^{-1}, respectively.

In a study of the possible intramolecular hydrogen bonding in neutral *o*-cresol, Rozas et al.[29] concluded that, in general, the methyl group cannot behave as a hydrogen bond acceptor. Our results indicate that hydrogen bonding to methyl groups is in fact possible in suitable systems. The main differences between the molecules studied are the ring size and the charge; given the conformational freedom of a larger ring and the stronger donor capacity of a protonated alcohol, hydrogen bonds to methyl groups can indeed be formed, even though they may be relatively weak.

Hydrogen Bonding to Alkanes

Hydrogen bonding to alkanes differs from conventional hydrogen bonding in that the acceptor is a bond rather than a lone pair or a similar source of electron density. Our NBO results establish that the predominant charge-transfer contribution is the interaction between σ_{OH}* and σ_{CH}, that is, the C−H σ-bond acts as an electron donor.

Olah[30] linked the basicity of alkanes to the σ-bond electrons, using the term sigma basicity to describe protonation of alkanes that involves the σ-bonds as the electron donors. A hydrogen bond to an alkane can be perceived as an incipient proton transfer to the C−H bond,[5] possibly resulting in cleavage of that bond, and formation of a carbocation and H_2. The bond length changes that accompany the formation of hydrogen-bonded alkane adducts can be rationalized in terms of the covalent contribution, as electron density is moved from the σ-orbital of the C−H bond into the σ*-orbital of the O−H bond. This transfer of electron density weakens the C−H as well as the O−H bonds and provides a rationale for the elongation of both and, in turn, the red shift of the associated stretching frequencies.[26]

Experiments[31] show that the protonation of alkanes preferentially occurs at C−H bonds of the more highly substituted

TABLE 4: Structural, Vibrational, and Energetic Properties by Intramolecular Hydrogen Bond Formation in Protonated Alcohols

		Δr_{OH}[a]	$\Delta \upsilon_{OH}$[a]	I_{OH}[a]	Δr_{CH}[a]	$\Delta \upsilon_{CH}$[a]	I_{CH}[a]	E_{stab}[b]
$(CH_3)_2CH(CH_2)_2OH_2^{+c}$	six-membered	0.002	46	1	0.009	115	4	3
$(CH_3)_2CH(CH_2)_3OH_2^{+c}$	seven-membered	0.019	403	4	0.022	243	4	13
$CH_3(CH_2)_4OH_2^{+d}$	eight-membered	0.018	384	4	0.018	145	5	0
$CH_3(CH_2)_5OH_2^{+e}$	eight-membered	0.023	483	5	0.021	226	6	4
$(CH_3)_2CH(CH_2)_4OH_2^{+c}$	eight-membered	0.027	555	6	0.025	254	4	8

[a] Changes with respect to the non-hydrogen-bonding O−H bond and with respect to the non-hydrogen-bonded all-trans conformer for the C−H bond; Å; B3LYP/6-31+G(d,p). [b] The stabilization calculated as the energy difference between the hydrogen-bonded and non-hydrogen-bonded conformers; kJ mol^{-1} G3//B3LYP. [c] CH group as an acceptor. [d] CH_3 group as an acceptor. [e] CH_2 group as an acceptor.

carbon atoms. This corresponds well with the trends exhibited by hydrogen-bonded alkane adducts, as the strongest hydrogen bonds are formed to the C−H bonds of the more highly branched carbon.

C−H bonds are not the only bonds capable of engaging in dihydrogen bonding. For example, the boron−hydride bonds in certain aminoborane adducts can also act as acceptors,[32] and there are structural similarities between these dihydrogen-bonded adducts and the alkane adducts of the present study, in particular the elongation of the acceptor bond, the asymmetric bifurcated hydrogen bond,[9,10,32] and the bent D−H···H−A geometry.[33]

Conclusion

Hydrogen bonding occurs in adducts of alkanes and protonated organic molecules. The calculated structural, vibrational, and energetic properties of adducts of alkanes and strong ionic acids are closely related to those of conventional hydrogen-bonded adducts. Alkane hydrogen bonding is strongest when involving a C−H bond at a tertiary carbon and strongly acidic donors. The results of NBO calculations show that the interactions include a covalent contribution derived from charge-transfer between the σ^*-orbital of the O−H bond in the donor and the σ-orbital of the acceptor C−H bond, in which the σ-electrons in the C−H bond act as the proton acceptor. One unusual aspect of alkane hydrogen bonding is that significant structural change takes place in the acceptor as well as in the donor, in particular, that both the O−H and C−H bonds undergo a considerable elongation, causing red shift of both O−H and C−H vibrational stretching frequencies. This deformation implies that the attractive forces within the adduct exceed the adduct stabilization by a significant amount. The hydrogen-bonded alkane adducts have a bent structure with the O−H bond pointing toward the middle of the C−H bond. Long-chain protonated alcohols exhibit intramolecular hydrogen bonding, which manifests itself in the same manner as the intermolecular hydrogen bonding, and can be equally strong.

Supporting Information Available: Sturctural, vibrational, and energetic properties of hydrogen bonded alkane adducts. This material is available free of charge via the Internet at http://pubs.acs.org.

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