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Ab Initio Study of the Structural, Energetic, Bonding, and IR Spectroscopic Properties of Complexes with Dihydrogen Bonds

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The results of an ab initio study of complexes with $X-H\cdots H-M$ dihydrogen bonds are presented. The proton donors include HCCH and its derivatives HCCF, HCCCl, and HCCCN; HCN and its derivatives $HCNLi^+$ and $HCNNa^+$; CNH, and H_2O , and the proton acceptor is LiH. For comparison, selected complexes with NaH as the proton acceptor have also been investigated. The structures, binding energies and harmonic vibrational frequencies of all complexes were obtained at the MP2/aug'-cc-pVTZ level of theory. The most stable complexes with C-H groups as proton donors are the cationic complexes $NaNCH^+:HLi$ and $LiNCH^+:HLi$. These complexes exhibit very short $H\cdots H$ distances and are prototypical of dihydrogen-bonded complexes that may dissociate by eliminating H_2 . The calculated binding energies correlate with the $H\cdots H$ distance, the elongation of the C-H donor bond, the amount of charge transfer into the $H\cdots H$ bonding region, and the charge density at the $H\cdots H$ bond critical point. As in conventional hydrogen-bonded complexes, the elongation of the proton donor C-H group correlates with the strength of the interaction, and with the red shift of the C-H stretching frequency. Although changes in the Li-H bond length do not follow a simple pattern, the Li-H stretching frequency is blue-shifted in the complexes.

Introduction

The subject of dihydrogen bonds has received a great deal of attention lately.^{1–8} The dihydrogen bond is an attractive intermolecular or intramolecular $H\cdots H$ interaction, arising from the close approach of an acidic proton and an hydridic hydrogen atom. If the hydridic hydrogen comes from a metal hydride, then the dihydrogen bond can be represented as $X-H\cdots H-M$, where X-H is the proton donor as in a conventional X-H-Y hydrogen bond, and MH is the proton-acceptor metal hydride. The first unequivocal evidence for the formation of a dihydrogen bond involving a metal hydride was presented independently by Crabtree, et al.,⁹ and Morris, et al.¹⁰ Very recently, Custelcean and Jackson¹¹ have published an excellent review article on dihydrogen bonding.

Given our long-standing interest in conventional hydrogen bonds, we have initiated a systematic investigation of a series of complexes stabilized by dihydrogen bonds. In this study, we have employed a correlated level of theory with a large, polarized basis set augmented with diffuse functions to determine the structures, binding energies, and bonding characteristics of these complexes. We have also investigated selected IR spectroscopic properties. Our attention will be focused primarily on complexes in which the dihydrogen bond involves a C-H group as the proton donor and LiH as the proton acceptor. Through chemical substitution the proton-donating ability of the C-H group will be varied, so that correlations among the

various properties of these complexes can be established, and trends elucidated. We will also investigate selected complexes in which the proton donor is CNH or H_2O , and the proton acceptor is NaH, to evaluate the dependence of the properties of dihydrogen-bonded complexes on the nature of X and M which form the $X-H\cdots H-M$ bond. Studies of the NMR one-bond $^1H-^1H$ and three-bond X-M spin-spin coupling constants across these $X-H\cdots H-M$ dihydrogen bonds will be reported in the following paper.

Methods

In this study, a systematic investigation of dihydrogen bonds has been carried out on complexes in which the proton donor is a C-H group and the proton acceptor is LiH. The proton donors include HCCH and its derivatives HCCF, HCCCl, and HCCCN; and HCN and its derivatives $HCNLi^+$ and $HCNNa^+$. A complex in which HCN is the proton donor to NaH has also been included, as well as complexes in which CNH and H_2O are proton donors to LiH and NaH. The structures of all monomers and complexes have been optimized at second-order Møller-Plesset perturbation theory (MP2)^{12–15} with Dunning's correlation-consistent polarized valence triple-split basis set on H, Li, and Na atoms, and this basis augmented with diffuse functions on C, N, F, O, and Cl atoms (aug'-cc-pVTZ).^{16–18} Calculations on HCCH:HLi which include diffuse functions on H atoms were carried out to test the sensitivity of structures and binding energies to the presence of such functions. The

TABLE 1: MP2/aug'-cc-pVTZ Optimized Geometries^a and Binding Energies (BE, kcal mol⁻¹) of Dihydrogen-Bonded Complexes

ZYXNCH·····HLi complexes										
	symmetry	M–H	H·····H	H–C	C–X (X = N, C)	X–Y	Y–Z	BE		
LiNCH ⁺ ·····HLi (1)	<i>C</i> _{∞v}	1.625 (1.602)	1.309	1.175 (1.072)	1.166 (1.159)	1.894 (1.953)		–27.1		
NaNCH ⁺ ·····HLi (2)	<i>C</i> _{∞v}	1.619	1.429	1.138 (1.070)	1.166 (1.161)	2.286 (2.354)		–23.7		
NCH·····HLi (3)	<i>C</i> _{∞v}	1.599	1.774	1.086 (1.065)	1.169 (1.167)	–		–8.8		
NCCCH·····HLi (4)	<i>C</i> _{∞v}	1.601	1.809	1.081 (1.063)	1.221 (1.217)	1.371 (1.372)	1.178 (1.177)	–8.1		
CICCH·····HLi (5)	<i>C</i> _{∞v}	1.600	1.930	1.075 (1.061)	1.216 (1.213)	1.643 (1.638)		–5.0		
FCCH·····HLi (6)	<i>C</i> _{∞v}	1.600	1.950	1.073 (1.060)	1.208 (1.205)	1.287 (1.280)		–4.8		
HCCH·····HLi (7)	<i>C</i> _{∞v}	1.599	1.978	1.074 (1.062)	1.215 (1.212)	1.062 (1.062)		–4.4		
NCH·····HNa (8)	<i>C</i> _{∞v}	1.921 (1.915) ^b	1.754	1.090 (1.065)	1.169 (1.167)			–9.7		
CNH·····HM Complexes										
	symmetry	M–H	H·····H	H–N	N–C	H–H–M	BE			
CNH·····HLi (9)	<i>C</i> _s	1.597	1.468	1.043 (0.998)	1.178 (1.177)	149.4	–14.2			
CNH·····HNa (10)	<i>C</i> _s	1.917	1.426	1.056	1.178	159.9	–15.8			
HOH·····HM Complexes										
	symmetry	M–H	H·····H	H–O	O–H	M–H–H	H–H–O	H–O–H	H–H–O–H	BE
HOH·····HLi (11)	<i>C</i> ₁	1.699	1.454	1.031 (0.961)	0.961	67.7	126.5	107.1 (104.1)	135.0	–18.6
HOH·····HNa (12)	<i>C</i> ₁	2.039	1.428	1.030	0.961	73.0	117.9	107.9	165.0	–15.7

^a Bond lengths in Å and bond angles in degrees. Monomer values are given in parentheses. ^b Na-H bond length.

optimized MP2/aug-cc-pVTZ H·····H distance is 1.974 Å, compared to the MP2/aug'-cc-pVTZ distance of 1.978 Å. The MP2 binding energies with these two basis sets are -4.5 and -4.4 kcal mol⁻¹ respectively. Hence, diffuse functions on H atoms are not required. No counterpoise corrections for basis-set superposition errors are needed with the aug'-cc-pVTZ basis set.¹⁹ MP2/aug'-cc-pVTZ harmonic vibrational frequencies were computed to establish that each monomer and complex corresponds to an equilibrium structure on the surface with no imaginary frequencies, and to obtain vibrational frequencies and band intensities.

Binding energies for these complexes have been computed as the difference between the total energy of the complex and the energies of the isolated monomers. The strengths of dihydrogen bonds have also been analyzed in terms of the topology of the electron density using the atoms-in-molecule theory of Bader.²⁰ For this purpose, we have located bond critical points (bcp) and have characterized these by their charge densities. In addition, because the formation of a dihydrogen bond involves polarization of the interacting systems and charge transfer, net atomic charges have been analyzed as a means of providing insight into the physics associated with the bond-formation process. For this analysis, we have employed the natural bond orbital (NBO) partitioning technique of Weinhold, et al.²¹ Optimization of the structures of all monomers and dihydrogen-bonded complexes, and calculation of harmonic vibrational frequencies were done using the Gaussian 98 program.²²

Results and Discussion

Geometries and Binding Energies. Table 1 presents the optimized structures of the dihydrogen-bonded complexes investigated in this study, along with the optimized monomer geometries for comparison. The equilibrium structures of all complexes in which C-H is the proton donor to LiH or NaH have *C*_{∞v} symmetry with a linear C-H·····H-M dihydrogen bond. As has been reported previously for dihydrogen-bonded complexes,¹⁻⁸ correlations can be found between structural properties such as intermolecular H·····H distances and changes in X-H distances, and binding energies. For the neutral complexes in which C-H is the proton donor and LiH the

proton acceptor (complexes 3-7 in Table 1), as the intermolecular H·····H distance decreases, the proton-donor C-H distance increases. If the donors are listed in order of increasing proton-donating ability to LiH (HCCH < HCCF < HCCCl < HCCCN < HCN), then the H·····H distance decreases from 1.978 Å in HCCH:HLi to 1.774 Å in NCH:HLi. The decrease in the H·····H distance is accompanied by an increase in the C-H distance from 0.012 Å in HCCH:HLi to 0.021 Å in NCH:HLi. The binding energies also increase from -4.4 kcal mol⁻¹ in the complex with HCCH as the proton donor, to -8.8 kcal mol⁻¹ in the complex with HCN as the donor. The correlations found for the dihydrogen-bonded complexes are similar to those observed in a series of closely related complexes stabilized by conventional (traditional) X-H·····Y hydrogen bonds. In such a series, as the X-Y distance decreases, the X-H distance and the binding energy increase.²³

The most stable complexes with C-H groups as proton donors are the cationic complexes NaNCH⁺:HLi and LiNCH⁺:HLi with binding energies of -23.7 and -27.1 kcal mol⁻¹, respectively. These complexes also have very short H·····H distances of 1.429 and 1.309 Å, and C-H distances that are elongated by 0.068 and 0.103 Å, respectively. The correlation between binding energies and H·····H distances, and binding energies and changes in C-H distances, are shown graphically in Figures 1 and 2, respectively. These data fit the equations

$$BE = -19.3r^2 + 99.37r - 124.85 \quad (1)$$

and

$$BE = 2812.7\Delta r_{CH}^2 - 568.13\Delta r_{CH} + 1.67 \quad (2)$$

where BE is the binding energy in kcal mol⁻¹, *r* in eq 1 is the H·····H distance, and Δr_{CH} in eq 2 is the change in the C-H distance in the complex. The correlation coefficients are 0.994 and 0.997, respectively. An equation similar to eq 1 has been reported by Grabowski⁴ for similar dihydrogen-bonded complexes.

Changes in the Li-H bond length upon complex formation do not follow a simple pattern. In the neutral complexes (3-7), there is a very slight shortening of the Li-H bond. This

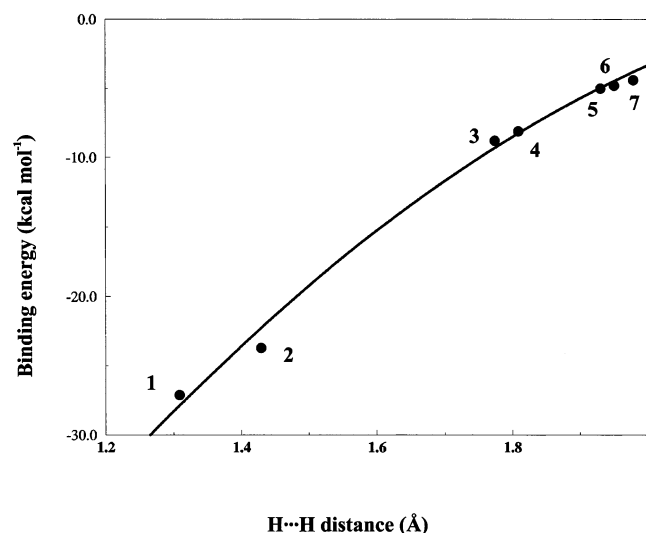


Figure 1. Binding energies of complexes with C-H...H-Li dihydrogen bonds versus H...H (r) distances. See Table 1 for numbering system.

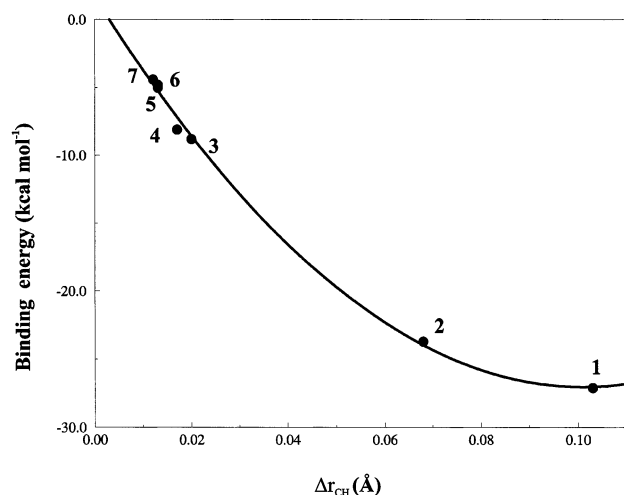


Figure 2. Binding energies of C-H...H-Li dihydrogen bonds versus changes in C-H distances (Δr_{CH}).

shortening was also observed previously by Grabowski.⁴ However, in the charged complexes (1 and 2) the Li-H bond elongates considerably. In neutral systems the hydrogen bond donor polarizes the charge distribution of LiH. As a result, the Li atom becomes more positively charged (Table 2), the charge density at the LiH bond critical point remains the same or increases slightly (Table 3), and the LiH bond shortens. This polarization is also mirrored in an increased negative charge on the hydridic hydrogen of LiH, ranging from 0.023 au in HCCH:HLi to 0.028 au in NCH:HLi. The situation is quantitatively different in the charged complexes, as evident from Tables 2 and 3. In the cationic complexes, there is a significant charge transfer from LiH toward the hydrogen bond donor, which depopulates the Li-H bonding region. This is reflected in a reduced charge density at the bond critical point, and a lengthening of the Li-H bond. This charge depletion is also reflected by a decrease of 0.009 and 0.049 au in the net charge on the hydridic hydrogen in $\text{NaNCH}^+:\text{HLi}$ and $\text{LiNCH}^+:\text{HLi}$, respectively. The net charge of the C-H proton increases by 0.035 to 0.040 au in the neutral complexes, but only by 0.026 and 0.008 au in $\text{NaNCH}^+:\text{HLi}$ and $\text{LiNCH}^+:\text{HLi}$, respectively.

It should also be expected that the interaction between the proton-donating and proton-accepting moieties should lead to

a mutual polarization of both systems, with charge transfer occurring from the proton acceptor (LiH) to the proton donor. Charge transfer from the proton acceptor to the proton donor is characteristic of conventional hydrogen bonds, and is evident for the dihydrogen-bonded complexes from the data of Table 2. In the neutral complexes the amount of charge transfer increases as the binding energy increases, varying from 0.014 au in HCCH:HLi to 0.033 au in NCH:HLi. In the cationic complexes, the amount of charge transfer is 0.119 and 0.163 au in $\text{NaNCH}^+:\text{HLi}$ and $\text{LiNCH}^+:\text{HLi}$, respectively. The correlation between binding energies and the amount of charge transfer is illustrated graphically in Figure 3. It should be noted that this correlation includes complex 8 which has NaH as the proton acceptor, and complex 9 with CNH as the proton donor to LiH.

Systematic changes in the charge densities at C-H and H...H bond critical points are also observed in these complexes, as can be seen from the data of Table 3. In the neutral complexes, as the binding energy increases, the charge density in the H...H dihydrogen bond also increases, from 0.013 e au^{-3} in HCCH:HLi to 0.019 e au^{-3} in NCH:HLi. At the same time, the electron density at the bond critical point in the C-H bond decreases by 0.005 e au^{-3} in HCCH:HLi to 0.013 e au^{-3} in NCH:HLi. By comparison, the electron densities at the H...H bond critical points in the cationic complexes are significantly greater at 0.042 and 0.055 e au^{-3} in $\text{NaNCH}^+:\text{HLi}$ and $\text{LiNCH}^+:\text{HLi}$, respectively. The electron densities decrease in the C-H bond by 0.049 and 0.071 e au^{-3} . These results suggest that the stability of a dihydrogen-bonded complex is related to the amount of charge transfer into the H...H bonding region. Indeed, the correlation between the stability of the complex and the electron density at the H...H bond critical point is nearly linear, as shown in Figure 4. Included among the data points is the NCH:HNa complex which has NaH as the proton acceptor. Among the neutral complexes with a C-H group as the proton donor, NCH:HNa has the largest binding energy, the greatest electron density at the H...H bond critical point, and the shortest H...H distance, as evident from Tables 1 and 3. This complex fits reasonably well with the correlations shown in Figures 3 and 4 for complexes with C-H...H-Li bonds.

Koch and Popelier²⁴ have characterized C-H...O hydrogen bonds in terms of the topology of the charge density. Our results indicate that dihydrogen bonds can be similarly characterized. In a dihydrogen bond, there exists a bond critical point which has a charge density that is typically an order of magnitude smaller than the charge density at the bond critical point of a covalent bond, and slightly smaller than the charge density at the bond critical point of a conventional hydrogen bond. Furthermore, in both conventional hydrogen bonds^{24,25} and dihydrogen bonds, a linear correlation exists between charge densities at bond critical points and binding energies.

Although the charge density at the H...H bond critical point for the equilibrium structures of complexes with C-H...H-Li bonds correlates with binding energy, this should not be interpreted to mean that this density is a maximum at the equilibrium distance. In fact, the density at the H...H bond critical point is related to the H...H distance, and continues to increase as the H...H distance decreases. This suggests that if the amount of electron density transferred is large enough, then the H-H distance could shorten to the distance in the H_2 molecule. Such is the case for linear $\text{HNCH}^+:\text{HLi}$, an obvious omission from the cationic complexes reported in Table 1. Optimization of the structure of this complex gives an H-H distance of 0.756 Å, which is quite close to that in the H_2

TABLE 2: NBO Net Charges (a.u.) of Dihydrogen-Bonded Complexes^a

ZYXNCH _a ·····H _b M complexes				
	<i>q</i> (M) (M = Li, Na)	<i>q</i> (H _b)	<i>q</i> (H _a)	Δq^b
LiNCH ⁺ ·····HLi (1)	+0.936 (+0.822)	−0.773 (−0.822)	+0.275 (+0.267)	0.163
NaNCH ⁺ ·····HLi (2)	+0.932	−0.813	+0.285 (+0.259)	0.119
NCH·····HLi (3)	+0.883	−0.850	+0.261 (+0.223)	0.033
NCCCH·····HLi (4)	+0.880	−0.853	+0.281 (+0.241)	0.027
CICCH·····HLi (5)	+0.864	−0.845	+0.276 (+0.238)	0.019
FCCH·····HLi (6)	+0.862	−0.846	+0.275 (+0.239)	0.014
HCCH·····HLi (7)	+0.860	−0.845	+0.260 (+0.225)	0.014
NCH·····HNa (8)	+0.866 (+0.786)	−0.825 (−0.786)	+0.265 (+0.223)	0.041

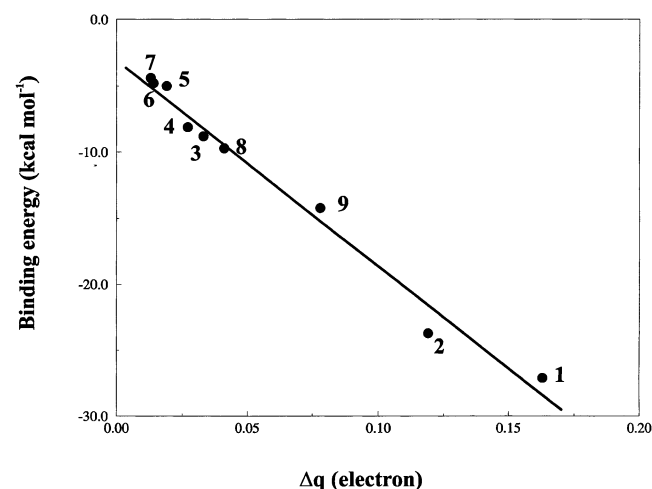
CNH _a ·····H _b M Complexes				
	<i>q</i> (M) (M = Li, Na)	<i>q</i> (H _b)	<i>q</i> (H _a)	Δq^b
CNH·····HLi (9)	+0.899 (+0.822)	−0.821 (−0.822)	+0.473 (+0.455)	0.078
CNH·····HNa (10)	+0.890 (+0.786)	−0.791 (−0.786)	+0.467	0.095

^a Monomer values are given in parentheses. ^b Charge transferred from the proton acceptor.TABLE 3: Charge Density (e au^{−3}) at Bond Critical Points of Bonds Directly Involved in the Dihydrogen Bond^a

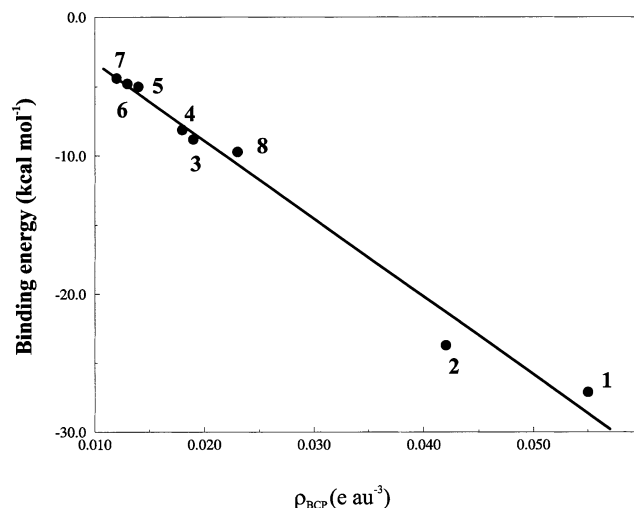
ZYXNCH·····HM complexes			
	M–H (M = Li, Na)	H·····H	H–C
LiNCH ⁺ ·····HLi (1)	0.035 (0.039)	0.055	0.227 (0.298)
NaNCH ⁺ ·····HLi (2)	0.036	0.042	0.250 (0.299)
NCH·····HLi (3)	0.039	0.019	0.286 (0.299)
NCCCH·····HLi (4)	0.039	0.018	0.292 (0.302)
CICCH·····HLi (5)	0.040	0.014	0.293 (0.300)
FCCH·····HLi (6)	0.040	0.013	0.293 (0.300)
HCCH·····HLi (7)	0.040	0.013	0.290 (0.295)
NCH·····HNa (8)	0.031 (0.032)	0.023	0.275 (0.329)

CNH·····HM complexes			
	M–H (M = Li, Na)	H·····H	H–N
CNH·····HLi (9)	0.040 (0.039)	0.036	0.292 (0.329)
CNH·····HNa (10)	0.031	0.041	0.278

HOH·····HM complexes			
	M–H (M = Li, Na)	H·····H	H–O
HOH·····HLi (11)	0.025 (0.039)	0.048	0.299 (0.366)
HOH·····HNa (12)	0.030 (0.032)	0.040	0.300

^a Monomer values are given in parentheses.Figure 3. Binding energies of complexes with dihydrogen bonds versus the amount of charge transfer (Δq) from the metal hydride.

molecule. However, this complex is not an equilibrium structure on the potential surface, but has two degenerate imaginary frequencies. This is an interesting result because it is known from experimental data that loss of H₂ can occur from

Figure 4. Binding energies of complexes with dihydrogen bonds versus the charge density at the H·····H bcp (ρ_{BCP}).

dihydrogen-bonded complexes.^{26–28} On the other hand, the formation of complexes with close H–H contacts and no H₂ loss have been described in both experimental^{29–32} and theoretical^{33–37} studies.

Table 1 also reports structures and binding energies for dihydrogen-bonded complexes with CNH as the proton donor to LiH and NaH. CNH is a stronger proton donor than NCH, with the result that binding energies of CNH:HLi and CNH:HNa are −14.2 and −15.8 kcal mol^{−1}, respectively. Thus, the binding energies, the electron densities at H·····H bond critical points, and the amount of charge transfer are greater, and the H·····H distances are shorter in the complexes with CNH compared to the corresponding complexes with HCN. As indicated above, the binding energy of the CNH:HLi complex fits the linear correlation between binding energy and charge transfer shown in Figure 3 for complexes with C–H·····H–Li bonds. Moreover, when the amount of charge transfer in CNH:HNa is used to estimate the binding energy from Figure 3, the value obtained (−17.7 kcal mol^{−1}), is in reasonable agreement with the ab initio calculated value (−15.8 kcal mol^{−1}). It should also be noted that the structures of complexes with CNH are not linear, but have C_s symmetry with H–H–Li and H–H–Na angles of 149.4° and 159.9°, respectively.

Data for complexes of LiH and NaH with H₂O are also reported in the tables. These complexes are asymmetric (C₁ symmetry), and are the most strongly bound neutral complexes.

TABLE 4: Selected Stretching Frequencies (cm^{-1}) and Intensities (km mol^{-1}) for Monomers and Dihydrogen-Bonded Complexes

ZYNCH.....HLi complexes				
	M-H (M = Li, Na) stretch		C-H stretch	
	frequency	intensity	frequency	intensity
LiNCH ⁺HLi (1)	1765 ^b (1424)	219 (221)	2353 ^b (3407)	490 (140)
NaNCH ⁺HLi (2)	1897 ^b	658	2452 ^b (3424)	1243 (130)
NCH.....HLi (3)	1494	527	3155 (3459)	734 (77)
NCCCH.....HLi (4)	1484	602	3196 (3473)	797 (84)
CICCH.....HLi (5)	1473	461	3295 (3490)	609 (91)
FCCH.....HLi (6)	1471	408	3324 (3509)	545 (96)
HCCH.....HLi (7)	1470	398	3302 (3437, 3525) ^c	421 (95, 9) ^c
NCH.....HNa (8)	1253 (1163) ^d	703 (282) ^d	3089 (3424)	1019 (130)
CNH.....HM complexes				
	M-H (M = Li, Na) stretch		N-H stretch	
	frequency	intensity	frequency	intensity
CNH.....HLi (9)	1523 (1424)	879 (221)	2996 (3813)	2362 (258)
CNH.....HNa (10)	1304 (1163)	1348 (282)	2785	3123
HOH.....HM Complexes				
	M-H (M = Li, Na) stretch		O-H stretch	
	frequency	Intensity	frequency	intensity
HOH.....HLi (11)	1300 (1424)	224 (221)	2658 (3825, 3953) ^c	1167 (8, 76) ^c
HOH.....HNa (12)	1087 (1163)	260 (282)	2065	1498

^a Monomer values are given in parentheses. ^b Highly coupled vibrations. ^c The first and second value correspond to the symmetric and the asymmetric stretching frequencies, respectively. Shifts are computed relative to the average of these two. ^d NaH stretch.

Thus, the stabilities of complexes with a given metal hydride increase with respect to the proton-donor group in the order C-H < N-H < O-H, an order also found for conventional hydrogen bonds. It is important to note that in the complexes with H₂O, the H-H-Li and H-H-Na angles are acute, with values of 67.7° and 73.0°, respectively. The bending of the metal of the metal hydride toward water would seem to favor a strong electrostatic attraction between the positively charged lithium or sodium atom and the negatively charged oxygen. Moreover, in this conformation, there is a favorable electrostatic interaction between the dipole moment of MH and the O-H bond dipole of H₂O. The structures of these complexes with elongated O-H and Li-H bonds and short H...H distances are suggestive of the nature of the reaction coordinate which might lead to dissociation of a dihydrogen-bonded complex to yield H₂.

Finally, it is interesting to note that the LiH complex with H₂O is more stable than the NaH complex, in contrast to the greater stability of NaH with HCN and CNH. Moreover, although the binding energy and the charge density in the dihydrogen bond are greater in HOH:HLi relative to HOH:HNa, the H...H distance of 1.454 Å in the more stable HOH:HLi complex is greater than the H...H distance of 1.428 Å in the less stable HOH:HNa.

IR X-H and M-H Stretching Frequencies. Table 4 presents X-H and M-H stretching frequencies for the complexes with X-H...H-M dihydrogen bonds that have been investigated in this study. As evident from Table 4, the X-H stretching frequency is lower and the intensity of the X-H stretching band is greater in the complex relative to the monomer. That is, the same IR spectroscopic signature of the shift to lower frequency and increase in intensity of the X-H stretching band upon formation of a traditional X-H...Y hydrogen bond is found for the X-H stretching band upon formation of an X-H...H-M dihydrogen bond. Moreover, for the entire set of complexes with C-H...H-M dihydrogen bonds, the frequency shift increases with increasing C-H distance and increasing binding energy of the complex. This

shift varies in the neutral complexes from -179 cm^{-1} in HCCH:HLi to -304 cm^{-1} in NCH:HLi and -335 cm^{-1} in NCH:HNa. The shifts in the cationic complexes are significantly larger at -972 cm^{-1} in NaNCH⁺:HLi and -1054 cm^{-1} in LiNCH⁺:HLi.

The shifts of the X-H stretching band also vary with the nature of the proton donor molecule. In complexes with LiH, the X-H shift increases from -304 to -817 to -1231 cm^{-1} when HCN, CNH, and H₂O are the proton donors, respectively. Similarly, for complexes with NaH, the shift in the X-H stretching band increases from -335 to -1028 to -1824 cm^{-1} , respectively, for the same set of proton donors. These shifts parallel the changes in X-H bond lengths upon dihydrogen bond formation. It is most interesting that these large shifts are found even in the complexes with H₂O as the donor, despite the very nonlinear X-H...H-M arrangement.

Changes in the Li-H and Na-H stretching frequencies in the dihydrogen-bonded complexes are not as systematic as those observed for the X-H stretching frequencies. In the neutral complexes with C-H...H-Li bonds, there is a very slight shortening of the Li-H bond, which leads to a blue shift of the LiH stretching frequency from 46 cm^{-1} in the complex with HCCH, to 70 cm^{-1} in the complex with HCN. Thus, the Li-H stretching frequencies tend to increase with increasing binding energy, but changes in the Li-H stretching frequencies do not correlate with distance changes. For example, the Li-H distances in HCCH:HLi and NCH:HLi are the same, but the Li-H stretching frequencies differ by 24 cm^{-1} . The Li-H stretching frequencies in the cationic complexes increase by 473 and 341 cm^{-1} , respectively. However, it is difficult to interpret these changes since the LiH vibrations in the cations are highly coupled to other vibrational modes.

In complexes with CNH as the proton donor, the N-H distance elongates by 0.045 and 0.058 Å whereas the N-H stretching frequencies decrease significantly by -817 and -1028 cm^{-1} when LiH and NaH, respectively, are the proton acceptors. These changes also reflect the increased binding energies of -14.2 and -15.8 kcal mol^{-1} , respectively. Once

again, the changes in the Li–H and Na–H distances and stretching frequencies do not exhibit systematic behavior. The Li–H distance decreases by 0.005 Å, whereas the Na–H distance increases by 0.002 Å. However, both Li–H and Na–H stretching frequencies increase by 99 and 141 cm⁻¹, respectively. Thus, Li–H and Na–H stretching frequencies in complexes with C–H...H–M and N–H...H–M bonds are systematically blue-shifted irrespective of whether the Li–H and Na–H distances increase or decrease.

In HOH:HLi and HOH:HNa, the O–H distances increase similarly by 0.070 and 0.069 Å, respectively, but the shifts in the O–H stretching frequencies are significantly different at –1231 and –1824 cm⁻¹, respectively. These shifts do not correlate with binding energies, since HOH:HLi has a greater binding energy than HOH:HNa. It must be remembered however, that in these two cases, in addition to the dihydrogen bond, there is also an electrostatic interaction between the metal and the oxygen atom, which leads to a large deviation of the O–H...H–M bond from linearity. The Li–H and Na–H distances increase by 0.097 and 0.124 Å in these complexes, and this leads to a decrease in the Li–H and Na–H stretching frequencies by 124 and 76 cm⁻¹, respectively.

Conclusions

Even though dihydrogen bonds are usually viewed as essentially electrostatic interactions, charge transfer into the H...H bonding region does occur. Moreover, when the interaction between the proton donor and proton-acceptor metal hydride is strong, as in complexes involving ionic species, there is a sizable charge transfer into the H...H bonding region. As the amount of charge transfer increases, the H...H distance decreases, approaching that in the H₂ molecule, and the complex could dissociate by eliminating H₂. In the series of complexes with C–H...H–Li dihydrogen bonds, the binding energy varies linearly with the amount of charge transferred, and the charge density at the H...H bond critical point.

The formation of a dihydrogen bond involves a systematic elongation of the X–H bond. As in conventional hydrogen-bonded complexes, this elongation increases with the strength of the X–H...H–M interaction, and the X–H stretching frequency is correspondingly red shifted in the complex. Changes in the M–H bond length of the proton acceptor do not follow a simple pattern, although the corresponding stretching frequencies appear systematically blue-shifted.

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