THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2005, *109,* 6137−6139
Published on Web 06/23/2005

Theoretical Investigation of the Weakly Dihydrogen Bonded Complexes FArCCH···HBeX (X = H, F, Cl, Br)

Mohammad Solimannejad*

Quantum Chemistry Group, Department of Chemistry, Arak University, 38156−879 Arak, Iran

Steve Scheiner

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

Received: May 13, 2005; In Final Form: June 7, 2005

An ab initio computational study of the properties of four linear dihydrogen-bonded complexes formed between the first compound with an Ar−C chemical bond (FArCCH) and HBeX (X = H, F, Cl, and Br) molecules was undertaken at the MP2/6-311++G(2d,2p) level of theory. The calculated complexation energy at MP2 and G2(MP2) levels decreases in the order HBeH···HCCArF > BrBeH···HCCArF > ClBeH···HCCArF > FBeH···HCCArF. The intermolecular stretching frequency, and shifts within the monomers, are compared with the energetic strength of complexation.

1. Introduction

The subject of dihydrogen bonds has received a great deal of attention lately.[1−6] The dihydrogen bond is an attractive intermolecular or intramolecular H···H interaction, arising from the close approach of a protonic H atom and a hydridic H atom. The evidence for the formation of dihydrogen bonds involving a metal hydride have been extensively presented.[7−11] Custelcean and Jackson[12] have published an extensive review of the structure, binding, and properties of dihydrogen bonds.

An ab initio study of HCCArF has recently appeared,[13] and the electronic structure of the HBeX (X = F, Cl, and Br) series has also been reported.[14] The negative partial charge on hydrogen in these HBeX hydrides,[14] coupled with the partial positive charge on hydrogen in HCCArF,[13] provides a primary condition for formation of dihydrogen bonds between these molecules. In the absence of an experimental search for these complexes up to the present, a theoretical analysis of their properties would appear to be in order. The present work thus reports a detailed examination of the stabilities, electronic structure, and vibrational frequencies of the title complexes.

2. Computational Details

Calculations were performed using the Gaussian03 system of codes.[15] Geometry optimizations and frequency calculations were performed at the MP2/6-311++G(2d,2p) level of theory. Harmonic vibrational frequency calculations were performed, which confirm the predicted structures as minima and evaluate zero-point vibrational energy (ZPE) corrections. The charge distribution has been analyzed by the natural bond orbital (NBO)[16] partitioning scheme at the MP2/6-311++G(2d,2p) level. The counterpoise (CP) method[17] was used to correct basis set superposition error (BSSE) in the calculation of the binding energy.

TABLE 1: MP2/6-311++G(2d,2p) Binding Energies and G2MP2 Thermodynamic Quantities (kJ/mol) of the Association Process of HCCArF with XBeH(X = H, F, Cl, Br)

	MP2/6-311++G(2d,2p)			G2MP2		
complex	D_e	BSSE	$D_e^{cp\ a}$	$\Delta E_0{}^b$	$\Delta H_0{}^c$	$\Delta G_{298}{}^d$
HBeH···HCCArF	−8.16	+1.54	−6.62	−6.23	−4.15	12.01
FBeH···HCCArF	−7.03	+2.54	−4.49	−4.84	−2.08	13.73
ClBeH···HCCArF	−7.11	+2.30	−4.81	−5.44	−2.62	13.45
BrBeH···HCCArF	−6.90	+1.91	−4.99	−5.81	−2.77	11.09

[a] D_e^{cp} refers to interaction energy after counterpoise correction, D_e + BSSE. [b] ΔE_0 is the G2MP2 energy of complexation at 0 K. [c] ΔH_0 represents the G2MP2 energy of the complexation processes including internal thermal energy. [d] ΔG_{298} is the G2MP2 Gibbs free energy of the complexation processes (at room temperature).

3. Results and Discussion

Association of the linear HCCArF with HBeX subunits leads to the linear $C_{\infty v}$ complexes XBeH···HCCArF (X = H, F, Cl, Br) that were calculated to be minima at the MP2/6-311++G(2d,2p) level of theory. Completely optimized geometries for all species studied in this work are given in Figure 1. The last three columns of Table 1 list the G2MP2 calculated thermodynamic properties for the association process of XBeH with HCCArF systems into XBeH···HCCArF.

Figure 1 reveals a number of intramolecular distortions that accompany the formation of the complex. The C−H covalent bond of HCCArF is lengthened by 0.002−0.003 Å, with a similar degree of stretching occurring in the more distant Ar−F bond. Concomitantly, there is a contraction of the C−Ar distance, by 0.005−0.009 Å. There are distortions in the HBeX subunit as well, including a small stretch in the H−Be bond. The Be−X bond is contracted, most notably the 0.006 Å reduction in Be−Br. With regard to the intermolecular distances, R(H···H) is shortest, at 2.097 Å for X = H, and longest for X

---

* Corresponding author. E-mail: m-solimannejad@araku.ac.ir.

10.1021/jp052534y CCC: $30.25

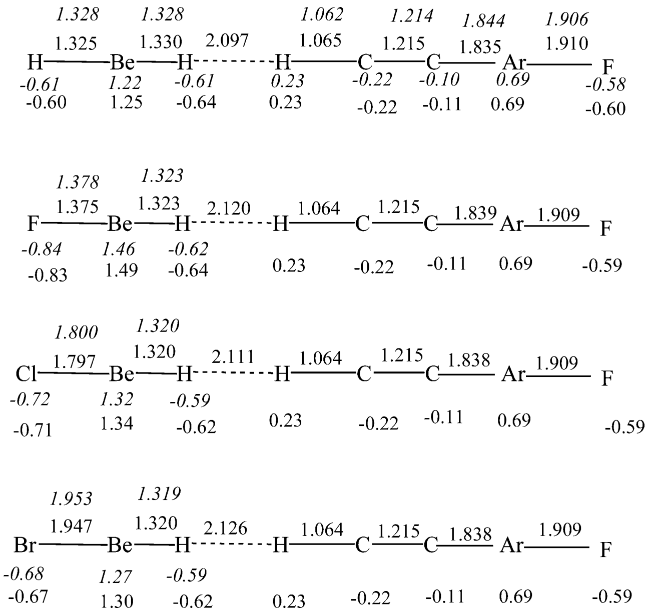

Figure 1. MP2/6-311++G(2d,2p) geometrical structures and NBO atomic charge (in proton charge) of XBeH···HCCArF (X = H, F, Cl, Br) complexes and monomers (italic numbers).

= Br, with an intermolecular distance of 2.126 Å. Note that the order of this particular distance varies as H < Cl < F < Br.

A search was conducted for other sorts of complexes that these two subunits might form. Allowing the H of the HBeX molecule to interact with the F end of the HCCArF molecule located minima, but these structures were of considerably higher energy, with binding energies on the order of 0.01 kJ/mol. Attempts to locate T-shaped structures were fruitless, as geometry optimization led to a complete restructuring of the entire complex.

The computed complexation energies of the linear dihydrogen bonded complexes XBeH···HCCArF, reported in Table 1, show that halogen substitution on beryllium decreases the stability of the complex, regardless of the level of theory. Also both levels of theory, MP2/6-311++G(2d,2p) and G2MP2, lead to the following conclusion concerning stability of complexes HBeH···HCCArF > BrBeH···HCCArF > ClBeH···HCCArF > FBeH···HCCArF.

The NBO charges reported in Figure 1 indicate little change in the atomic charges upon complexation. As a corollary, there would appear to be very little charge transfer between the two moieties.

TABLE 3: MP2/6-311++G(2d,2p) Unscaled Vibrational Frequencies (cm^{-1}) of XBeH (X = H, F, Cl, Br) and HCCArF Monomers

frequency	HCCArF	HBeH	FBeH	ClBeH	BrBeH
$\omega_{1,2}$	104(π)	742(π)	587(π)	547(π)	531(π)
ω_3	339(π)	2077(σ)	1189(σ)	823(σ)	697(σ)
ω_4	339(π)	2285(σ)	2241(σ)	2236(σ)	2231(σ)
ω_5	339(σ)				
ω_6	562(σ)				
$\omega_{7,8}$	660(π)				
ω_9	2031(σ)				
ω_{10}	3466(σ)				

TABLE 4: MP2/6-311++G(2d,2p) Stretching Frequencies and Shifts (cm^{-1})

X	$\Delta\nu$(Be−H)	$\Delta\nu$(Be-X)	$\Delta\nu$(C−H)	ν_σ[a]
H	8	11	−40	85
F	11	16	−29	54
Cl	8	17	−30	46
Br	6	15	−31	37

[a] Intermolecular stretching frequency.

The harmonic vibrational frequencies of the complexes, and their constituent monomers, are listed in Tables 2 and 3. The calculated frequencies confirm (there is no imaginary frequency) that structures with $C_{\infty v}$ symmetry are minima in the potential energy surfaces (PESs) of the title complexes.

It was noted above that the H−Be bond of HBeX is stretched and Be−X shortened by the complexation. The vibrational data indicate that the stretching frequencies associated with both of these bonds (ω_{18} and ω_{16}) are shifted to the blue, as reported in Table 4. On the other hand, the stretching of the H−C bond of HCCArF (ω_{19}) is accompanied by a red shift. The magnitude of this shift is greatest (40 cm^{-1}) for HBeH, as compared to 29−31 cm^{-1} for the various substituted XBeH molecules, placing this shift in rough correspondence with energetic strength of the interaction. Another correlation with the energetics is noted for ω_3 in the dimer, the intermolecular stretching vibration, ν_σ. This frequency is equal to 85 cm^{-1} for the HBeH complex but is in the smaller range of 37−54 cm^{-1} for the various XBeH complexes. The X = F complex has the highest frequency in this range, and X = Br the lowest, which is not in full consonance with the MP2/6-311++G(2d,2p) values of D_e, wherein X = Cl is associated with the strongest bond of the three, albeit only by a little. This discrepancy may be connected with the heavier mass of Cl, as compared to F, which would tend to diminish the vibrational frequency.

The reported values of ΔE_0, ΔH_0, and ΔG_{298} (Table 1) for the association process of XBeH + HCCArF → XBeH···HCCArF indicate that the dihydrogen-bonded complexes ought to be experimentally observable in the gas phase, certainly at low temperature. It is our hope that the present study may

TABLE 2: MP2/6-311++G(2d,2p) Unscaled Vibrational Frequencies (cm^{-1}) of XBeH···HCCArF (X = H, F, Cl, Br) Complexes

frequency	HBeH···HCCArF	FBeH···HCCArF	ClBeH···HCCArF	BrBeH···HCCArF
$\omega_{1,2}$	23(π)	22(π)	16(π)	11(π)
ω_3	85(σ)	54(σ)	46(σ)	37(σ)
$\omega_{4,5}$	97(π)	86(π)	64(π)	54(π)
$\omega_{6,7}$	161(π)	158(π)	143(π)	137(π)
$\omega_{8,9}$	344(π)	345 (π)	344(π)	343(π)
ω_{10}	353(σ)	349(σ)	350(σ)	350(σ)
ω_{11}	555(σ)	558(σ)	543(π)	523(π)
ω_{12}	723(σ)	613(π)	543(π)	523(π)
ω_{13}	723(σ)	613(π)	557(σ)	557(σ)
ω_{14}	764(π)	759 (π)	761(π)	712(σ)
ω_{15}	764(π)	759 (π)	761(π)	744(π)
ω_{16}	2029(σ)	1205(σ)	840(σ)	744(π)
ω_{17}	2088(σ)	2029(σ)	2029(σ)	2030(σ)
ω_{18}	2293(σ)	2252(σ)	2244(σ)	2237(σ)
ω_{19}	3426(σ)	3437(σ)	3436(σ)	3435(σ)

motivate experimentalists to search for the title complexes, perhaps by matrix isolation techniques. It may also be possible to observe stable complexes formed between HCCArF and other hydrides such as $H_{2-n}X_nAlH\cdots HCCArF$ ($n = 0-2$; X = F, Cl, Br).

References and Notes

(1) Popelier, P. L. A. *J. Phys. Chem. A* **1998**, *102*, 1873.

(2) Alkorta, I.; Rozas, I. E. J. *Chem. Soc. Rev.* **1998**, *27*, 163.

(3) Berski, S.; Lundell, J.; Latajka, Z. *J. Mol. Struct.* **2000**, *552*, 223.

(4) Grabowski, S. J.; Robinson, T. L.; Leszczynski, J. *Chem. Phys. Lett.* **2004**, *386*, 44.

(5) Grabowski, S. J.; Sokalski, W. A.; Leszczynski, J. *J. Phys. Chem. A* **2004**, *108*, 1806.

(6) Grabowski, S. J. *J. Mol. Struct.* **2000**, *553*, 151.

(7) Crabtree, R. H. *Science* **1998**, *282*, 2000

(8) Cybulski, H.; Pecul, M.; Sadlej, J. *J. Chem. Phys.* **2003**, *119*, 5095.

(9) Alkorta, I.; Elguero, J.; Mó, O.; Yáñez, M.; Del Bene, J. E. J. *Phys. Chem. A* **2002**, *106*, 9325.

(10) Del Bene, J. E.; Perera, S. A.; Bartlett, R. J.; Alkorta, I.; Elguero, J.; Mó, O.; Yáñez, M.; J. *Phys.* Chem. A **2002**, *106*, 9331.

(11) Solimannejad, M.; Boutalib, A. *Chem. Phys. Lett.* **2004**, *389*, 359.

(12) Custelcean, R.; Jackson, J. E. *Chem. Rev.* **2001**, *101*, 1963.

(13) Cohen, A.; Lundell, J.; Gerber, R. B *J. Chem. Phys* **2003**, *119*, 6415.

(14) McDowell.; S. A. C. *J. Mol. Struct (THEOCHEM)* **2002**, 593, 33.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B02; Gaussian, Inc.: Pittsburgh, PA, 2003.

(16) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 269.

(17) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, 19, 553.