casite structure is included in the pyrite class. The pyrite $Co(S_xSe_{1-x})_2$ exhibits a positive deviation from Vēgard's law,[54] consistent with the packing mismatch argument given for layered materials. However, the mixed-cation pyrites behave quite differently from their layered counterparts. The systems $Fe_{1-x}Ni_xTe_2$ and $Fe_{1-x}Co_xTe_2$[55] both show positive deviations from Vēgard's law. The dual series $Fe_{1-x}Co_xS_2$ and $Co_{1-x}Ni_xS_2$ show negative deviation if one plots the cubic a parameter vs. the number of electrons[56] from FeS_2 to NiS_2. If the linear behavior of $Fe_{1-x}Co_xS_2$ is extrapolated to NiS_2, this deviation can be viewed as a positive deviation for the nickel compound, and it is further indicated by the return to the $Fe_{1-x}Co_xS_2$ volume increase when additional atoms are added in the $Ni_{1-x}Cu_xS_2$ series. We feel the unusual behavior seen in the mixed-cation pyrites when compared to that of layered materials is a result of both the higher atomic density and the chalcogen–chalcogen bond present in the pyrites. This implies greater dependence of binding energy on structure and vice versa. When the atomic density of a pyrite is decreased, behavior closer to that of the layered materials is expected. This is apparently seen in the $Cu(S_xSe_{1-x})_2$ and $Cu(Se_xTe_{1-x})_2$ materials where the low-density copper pyrites exhibit negative deviation from Vēgard's law[57] similar to that seen in the platinum systems. Such speculation would be answered by study of several mixed-structure systems, for example, the low-pressure phases of $Fe_{1-x}Ni_xTe_2$.

Some final comments and cautions on mixed dichalcogenides are in order. The synthetic details affect the homogeneities and stoichiometry of the product. Transport and mineralization reactions can improve stoichiometry but adversely affect both purity and homogeneity. Crystal quality can also be a function of composition. $Hf(Se_xTe_{1-x})_2$ exhibits good quality crystals for end members but poor crystal formation for intermediate compositions. The opposite is true for $Mo(S_xSe_{1-x})_2$.[58] Finally, one must remember that since most preparations are quenched from high temperature, the products reflect the thermodynamics at the growth temperature. This most likely explains the surprising lack of superstructure observed in these materials.

Acknowledgments. We thank Wayne Fisher, Lynn Schneemeyer, and Angy Stacy for their helpful suggestions. This research was sponsored by the U.S. Air Force, Office of Scientific Research, Grant No. 80-0009, and was supported in part by the National Science Foundation and the Cornell University Materials Science Center.

Registry No. $HfSe_2$, 12162-21-9; $HfTe_2$, 39082-23-0.

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Theoretical Study of the Structure and Stability of Oligomers of LiH

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The structure and stability of oligomers of lithium hydrides, $(LiH)_n$ ($n \leq 8$), have been investigated by ab initio computations. Geometries are optimized by the energy gradient method. The calculation confirms as expected the strong tendency of lithium hydride to oligomerize. The equilibrium structure for the oligomers with the odd number of n is found to be planar cyclic with D_{nh} molecular geometry. On the other hand, the three-dimensional structures become more stable than the planar ones for oligomers with the even number of n, which point to the crystal structure. The features of geometrical parameters are also discussed in connection with the ionic character of the Li–H bond.

Introduction

The crystalline lithium hydride is a cubic system with a bond length of 2.045 Å, and it is known as a typical ionic crystal.[1c] However, relatively few experimental and theoretical investigations of oligomers of LiH have been published until now. Experimentally only the dimer is identified by mass spectrometry and its atomization energy determined.[2] Theoretical studies[3-5] have reported on the oligomers $(LiH)_n$ ($n \leq 4$), and they predict planar cyclic structures with D_{nh} molecular symmetry although for the tetramer a three-dimensional T_d structure shows a comparable stability to the D_{4h} structure. More recently we have studied[6] small lithium hydrides, Li_nH_m ($m \leq n \leq 4$), theoretically by referring to mass spectroscopic results of Li clusters[7] and found that the lithium hydrides are stabilized by hydrogenation and that the oligomers of lithium hydrides, $(LiH)_n$, are the most stable compounds in the series of Li_nH_m. We have also investigated the structure and the stability of the hexamer of LiH optimized by the energy gradient method.[8] For the energy minimum configurations, we found the structural principle that the anion–anion distances are greater than those of cations, which causes the highly distorted three-dimensional structures.

In the present paper, we will report theoretical ab initio computations for the oligomers of lithium hydride, $(LiH)_n$ ($n \leq 8$). We want to make clear the following problems: First, what are the equilibrium structures of the oligomers of the ionic molecules? Second, how large is the stabilization energy

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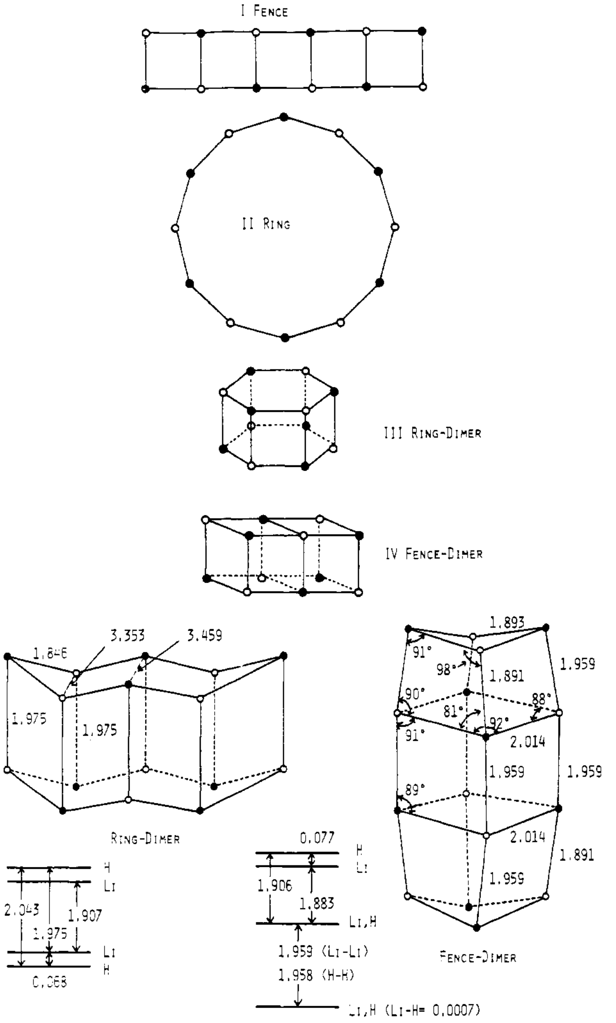


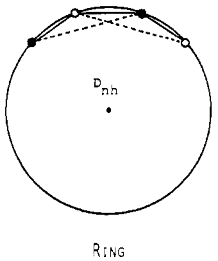
Figure 1. Structural models of $(LiH)_6$: ○, Li atom; ●, H atom.

for the clustering reactions? With these studies, we want to derive the general features of the ionic oligomers.

Table I. Total Energy (au) for the Optimized $(LiH)_n$

n	I fence	II ring	III ring dimer	IV fence dimer
1	−7.97718			
2	−16.02425			
3^a	...	−24.07910		
4	−32.11128	−32.12550	−32.11962	
5^b	−40.15308	−40.16819		
6	−48.18936	−48.20816	−48.22040	−48.21481
7	−56.22048	−56.24820		
8	−64.26105	−64.28699	−64.31364	−64.30885

^{a} There is no local minimum for the fence structure for $(LiH)_3$. ^{b} The side-ring-dimer structure for $(LiH)_5$ gives −40.15128 au.



n	Li-H	Li-Li	H-H
2	1.819	2.405	2.731
3	1.790	2.966	3.205
4	1.745	3.081	3.338
5	1.736	3.189	3.388
6	1.738	3.264	3.426
7	1.725	3.292	3.414
8	1.718	3.308	3.407

Figure 2. Optimized geometries of some oligomers of lithium hydride. Bond distances are in Å.

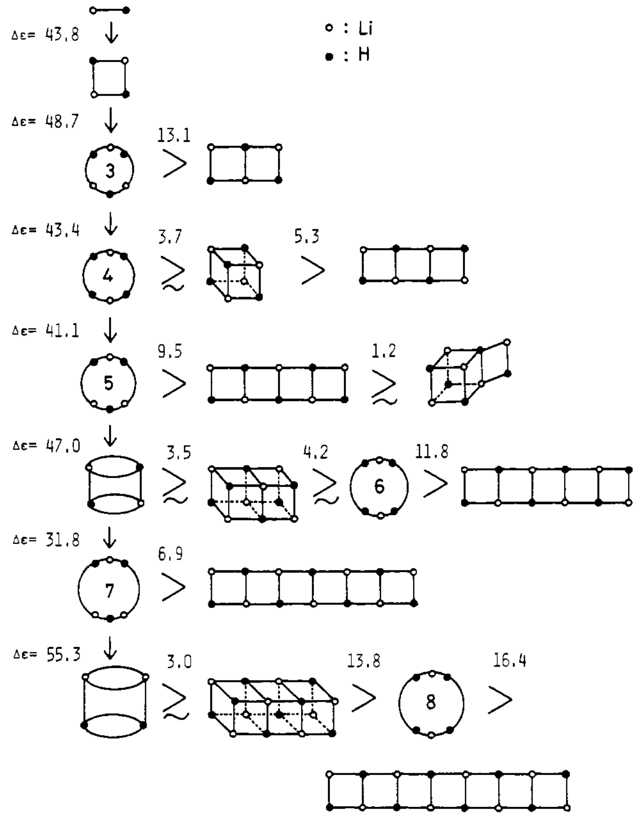


Figure 3. Diagram for the structure and stability of $(LiH)_n$. The most stable model is given on the left side for each oligomer. The stability decreases from left to right. Values are the energy differences in kcal/mol between each two structural models for the same oligomers. The $\Delta\epsilon$ is the heat of reaction given by $(LiH)_{n-1} + LiH = (LiH)_n + \Delta\epsilon$.

Computational Details

The four kinds of structures considered here are shown in Figure 1. They are named as fence, ring, fence dimer, and ring dimer respectively. The fence structure is planar and consists of a chain of LiH units with antiparallel arrangement. The ring structure is planar cyclic with D_{nh} molecular geometry. We have checked that these planar structures are stable with respect to the out-of-plane distortions. We have also considered three-dimensional structures. They are fence-dimer and ring-dimer structures. The fence-dimer model is chosen in accordance with the cubic crystal structure of LiH. We optimized the geometries of these four structures by the energy gradient method.[9]

Previous studies[3-6] show that the electron correlation effect has rather small influence on the relative stabilities of the above four models[10] and on the heats of reactions. So the present calculations were mostly carried out on the SCF level. We used the GAUSSIAN 70[11] and HONDO[12] programs. The 5-21G basis set[13] was used on the lithium atom and a (4s) primitive Gaussian basis contracted to [2s] was used on the hydrogen atom.[14] This basis set gives slightly longer bond distances compared to the experimental ones.

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Table II. Bond Distance and Number of Counterions for $(LiH)_n$

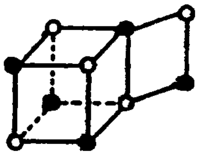
	bond dist rel to that in cryst, %	no. of counterions surrounding each ion
LiH (monomer)	80	1
ring	84–89	2
fence	88–91	2, 3
ring dimer	90–97	3
fence dimer	92–100	3, 4
crystal[a]	100	6

[a] The experimental Li-H distance is cited.

Results and Discussions

Table I summarizes the total energies for the oligomers of LiH. Optimized geometries for the ring structure and ring-dimer and fence-dimer structures for octamers are shown in Figure 2. The relative stability is schematically described in Figure 3. In the figure, the most stable model is given on the left side for each oligomer; the stability decreases from left to right. We also list the energy difference in kcal/mol between each two structures.

When n is the odd number such as the trimer, pentamer, and heptamer, the lowest energy was obtained for the ring structure. The energies for the fence models are more than 10 kcal/mol above the ring energies. For these oligomers, the dimer-type structures become unstable due to the repulsive Coulomb forces in the directly bonded cation–cation and anion–anion structures. So we considered the alternative structure called the side-ring dimer obtained from the ring dimer by addition of a LiH. This structure for $(LiH)_5$ shows a comparable stability to the fence structure. This also confirms that the planar cyclic structure with D_{nh} is energetically favorable for the oligomers with an odd number of n.



side-ring dimer
for $(LiH)_5$

On the other hand, the dimer structures become more stable than the planar ones for the even number of n. For the tetramer, the three-dimensional T_d structure has nearly the same energy as the D_{4h} ring structure as indicated by the previous studies.[4] The fence dimer is only 4 kcal/mol lower in energy than the ring structure for the hexamer, but the former becomes clearly more stable (14 kcal/mol) than the latter for the octamer. Thus, the stability of the three-dimensional structures increase with the increase of n. For the hexamer and octamer, the ring-dimer structure gives lower energy than the fence dimer. However, we can see the tendency that the fence dimer becomes more and more favorable with increasing n: the energy difference between the two models for the octamer falls off to only 3.0 kcal/mol. Here we should point out that the fence-dimer structure can be derived from the ring-dimer structure. That is, as a result of attractive or repulsive Coulomb forces between ions, the transition from one structure to another can easily be expected. Thus we would anticipate that the fence-dimer structure may become more and more favorable with the increase of n and that the oligomers for sufficiently large n have structures with a coordinate number of six as in the crystal.

Now let us discuss some features of the geometrical parameters. We found that the anion–cation distances for each model show little variation with the number of n and depend mainly on the structural models. We summarized in Table II the optimized Li–H bond distance in percent relative to the experimental one in the crystal with the number of counterions surrounding each ion. The shortest distance is found for the monomer (about 80% of the corresponding distance in the crystal). On the other hand, the largest distance is found for the three-dimensional structures (90%–100%). The bond distance for the planar structures is in between (84–91%). The number of counterions surrounding each ion increase in the order monomer, planar structures, three-dimensional structures. These geometrical trends are consistent with our chemical intuition. That is, the covalent character of the Li–H bond decreases (or increases of ionic character) in the order monomer, planar structures, three-dimensional structures.

Table III. Stabilization Energy per LiH Molecule (kcal/mol)

n	I fence	II ring	III ring dimer	IV fence dimer
2	21.9			
3	26.6	30.9		
4	31.8	34.0	33.1	
5	33.5	35.4		
6	34.1	36.1	37.4	36.8
7	34.1	36.6		
8	34.8	36.8	38.9	38.5

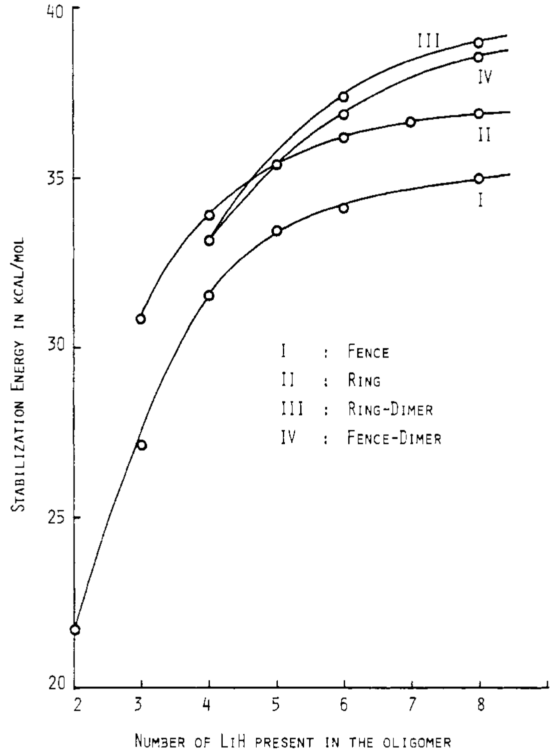


Figure 4. Stabilization energy per LiH unit.

Another interesting feature is that the anion–anion distance is greater than that of cations for each oligomer. This trend can typically be verified in the optimized ring structures given in Figure 2. Now let us discuss the optimized fence-dimer and ring-dimer structures of $(LiH)_8$ shown in Figure 2. In the fence dimer, the two outside $(LiH)_2$ groups become nonplanar rhombuses, and the central $(LiH)_4$ group forms an approximate cube, in which the Li–H distances are 2.014 and 1.959 Å, respectively, and the bond angles are near 90° (±2°). As to the ring dimer, the ring composed of the $(LiH)_4$ group is separated into two rings. The ring of Li_4 is located at the inner side and that of H_4 at the outer side. This structure of $(LiH)_4$ resembles the crown-type structure. These geometrical characteristics agree with the suggestions of our previous paper.[8]

Table IV. Dimerization Energy (kcal/mol)

$2\mathrm{LiH} = (\mathrm{LiH})_2$	43.8
$2(\mathrm{LiH})_2(D_{2h}) = (\mathrm{LiH})_4(T_d)$	44.7
$2(\mathrm{LiH})_3$(ring) = $(\mathrm{LiH})_6$(ring dimer)	39.0
$2(\mathrm{LiH})_3$(ring) = $(\mathrm{LiH})_6$(fence dimer)	35.5
$2(\mathrm{LiH})_4$(ring) = $(\mathrm{LiH})_8$(ring dimer)	39.2
$2(\mathrm{LiH})_4$(fence) = $(\mathrm{LiH})_8$(fence dimer)	54.2

Table V. Calculated Ionization Potentials for $(\mathrm{LiH})_n$ in eV

n	fence	ring	ring dimer	fence dimer
1	8.13			
2	8.40	8.40		
3	8.06	9.32		
4	8.19	9.51	9.08	9.08
5	8.23	9.70		
6	8.57	9.74	9.03	8.85
7	8.15	9.80		
8	8.29	9.82	9.03	8.62

Table III shows the stabilization energies per LiH unit estimated by the equation

$$\Delta E = [nE(\mathrm{LiH}) - E(\mathrm{Li}_n\mathrm{H}_n)]/n$$

The stabilization energies are also shown in Figure 4 plotted vs. the number of LiH groups present in the oligomers. The stabilization energy in any structual model is found to increase with n. Particularly, the stabilities in the ring-dimer and fence-dimer structures become high with the increase of n. This indicates a strong tendency of LiH to oligomerize acceleratively and rationalizes an initial stage of the growth of the crystal. For the crystal, the heat of sublimation is 52.6 kcal/mol.[15] So our calculation reproduces the experimental trend qualitatively but underestimates the magnitude of the stabilization energy.

Figure 3 also shows heats of reactions, given by the equation

$$(\mathrm{LiH})_{n-1} + \mathrm{LiH} = (\mathrm{LiH})_n + \Delta\epsilon$$

The calculated heats of reactions are around 40 kcal/mol, which implies that the above reactions are exothermic and readily occur. We also evaluated the dimerization energy for each step and summarized them in Table IV. The dimerization energy of the ring structure is smaller than the corresponding heat of reaction in Figure 3. In addition, if we take account of the low probability of the multicenter reaction for the dimerization, we may conclude that the above clustering reactions are more preferable than the dimerization reactions.

In Table V, we give ionization potentials (IP's) for the oligomers of LiH approximated by Koopmans' theorem. The calculated IP for the monomer of 8.13 eV should be compared to the experimental IP of 7.7 eV. The estimation via Koopmans' theorem is a little too high, reflecting the decrease in the magnitude of the electron correlation on ionization. For the fence structure, the IP's show little variation with n and average ca. 8.25 eV. For the ring structure, however, the IP values for $(\mathrm{LiH})_n$ increase with the increase of n. For oligomers in fence-dimer structures with the even number of n, the magnitude of IP's decreases with n, which is anticipated to be the case for the crystal.

Finally, let us examine the ionic character of the oligomers of LiH in terms of the density maps. Figure 5 describes the electron contour maps for Li_2, LiH, $(\mathrm{LiH})_2$, and $(\mathrm{LiH})_6$ with the net charges on H and Li atoms. The accumulation of electron charge on hydrogen leads to rather spread out or diffuse charge distribution for the anion, which is in contrast to the compact charge distribution for the cation. This leads to the structural principle that the anion–anion distances are always found to be greater than those of cations. The rectangular parts appearing in the center of the $\mathrm{Li}_2\mathrm{H}_2$ fragment correspond to the valley, not the hill; these parts indicate electron-deficient parts. Thus, we see that there is no bonding between nearest anion and anion and between cation and cation. In the fence structure, the degree of the polarization of the inner LiH bond is larger than that of the outer LiH bond. This also reflects the ionic character of the bond and therefore may depend on the number of counterions.

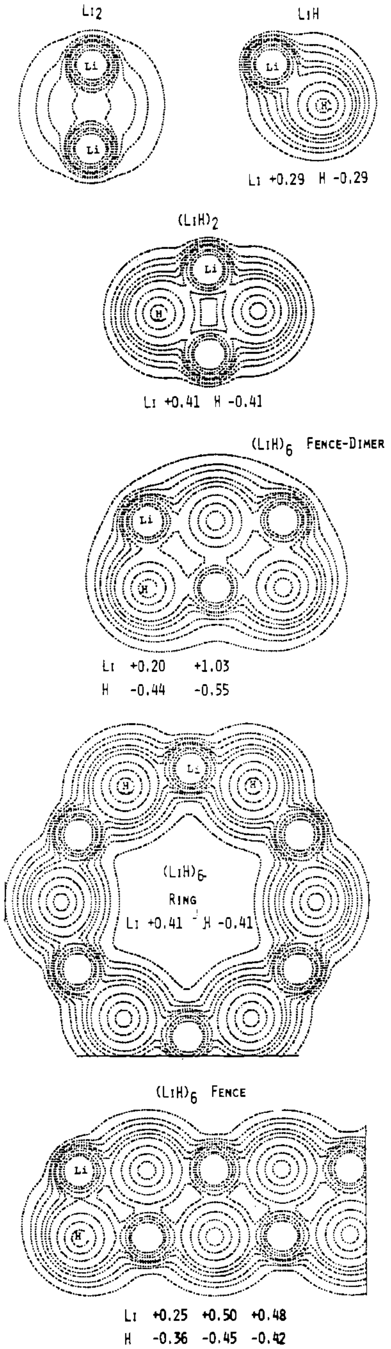


Figure 5. Electron density contour maps of LiH, $(\mathrm{LiH})_2$, and $(\mathrm{LiH})_6$.

In conclusion, the computations reported in the present paper predict as expected the strong tendency of lithium hydride to oligomerize. The equilibrium structure for the oligomer with an odd number of n is the planar cyclic, and three-dimensional structures are found to become more stable than the planar structures for an even number of n. From the viewpoint of the number of the counterions surrounding each ion, the fence-dimer and ring-dimer structures presented here

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are still far from being good models for the ionic crystal. However, we can find some aspects in the geometrical parameters and IP's for the oligomers that point already to those properties in the crystal.

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Registry No. LiH, 7580-67-8; $(LiH)_2$, 78715-95-4; $(LiH)_3$, fence, 78715-96-5; $(LiH)_3$, ring, 65219-65-0; $(LiH)_4$, fence, 78715-97-6; $(LiH)_4$, ring, 78715-98-7; $(LiH)_4$, ring dimer, 78715-99-8; $(LiH)_5$, fence, 78716-00-4; $(LiH)_5$, ring, 78716-01-5; $(LiH)_5$, fence, 78716-02-6; $(LiH)_6$, ring, 78716-03-7; $(LiH)_6$, ring dimer, 78716-03-7; $(LiH)_6$, ring dimer, 78716-04-8; $(LiH)_6$, fence dimer, 78716-05-9; $(LiH)_7$, fence, 78716-06-0; $(LiH)_7$, ring, 78716-07-1; $(LiH)_8$, fence, 78716-08-2; $(LiH)_8$, ring, 78716-09-3; $(LiH)_3$, ring dimer, 78716-10-6; $(LiH)_8$, fence dimer, 78716-11-7.

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Structures of Complex Beryllium Hydrides and Fluorides, $LiBeX_3$ and Li_2BeX_4

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Alternative structural possibilities for $LiBeX_3$ and for Li_2BeX_4 (X = H or F) monomers were examined at various levels of ab initio molecular orbital theory. For $LiBeX_3$, there is a decided preference for attachment of lithium at the edges of BeX_3 triangles (II), rather than to corners (I) or to faces (III). For Li_2BeX_4, the results are not as clear-cut. At the highest theoretical level employed, MP2/6-31G*//4-31G, Li_2BeH_4 prefers lithium attachment to two faces of a BeH_4 tetrahedron (VII); the opposite edge arrangement (V) is next best energetically. Planar six-membered ring structures (IV) for both Li_2BeF_4 and Li_2BeH_4 are preferred at the 4-31G//4-31G level (the highest feasible for the former species). The corresponding anions BeX_3^- and BeX_4^{2-} (in both planar and tetrahedral geometries) were also examined, and the energies of various possible dissociation reactions were calculated.

Introduction

Analogous to boron and aluminum which form the well-known complex hydrides and fluorides MBX_4 and $MAlX_4$, beryllium also forms similar complex salts with alkali metals, nMX·BeX_2 (n = 1 or 2).[2-7] The 1:1 complexes, e.g., $LiBeH_3$[5] and $LiBeF_3$,[4,7] are simplest; 2:1 complexes (Li_2BeH_4[5] and Li_2BeF_4[4,6,7]) also are known. Li_2BeF_4 is of technical interest; its molten salt might find use as a superior cooling and breeding agent in nuclear technology, especially in fusion reactors.[8]

The infinite-lattice crystal structures of these species are well established.[4-6] Moreover, the existence of monomeric $LiBeF_3$ and Li_2BeF_4 in the gas phase has been demonstrated mass spectroscopically.[3b] IR studies by Snelson and Cyvin[4] on matrix-isolated monomeric species led to the interesting and unusual proposal that planar IV, rather than an alternative, tetrahedral BeF_4-based geometry, represented the structure of Li_2BeF_4.

We have examined various structural possibilities for $LiBeH_3$, Li_2BeH_4, $LiBeF_3$, and Li_2BeF_4 by means of ab initio molecular orbital calculations. The parent anions, BeH_3^-, BeH_4^{2-}, BeF_3^-, and BeF_4^{2-}, were also included in this study. Structures of $LiBeH_3$ and $LiBeF_3$ have been calculated before;[9,10] for uniformity, we reexamined these species employing higher levels of theory.

Computational Methods

The structures of the fluorides and hydrides were first optimized with use of the minimal STO-3G basis set.[11] Geometry optimizations were then carried out with the small split-valence basis 4-31G[12a] (5-21G for lithium and beryllium is implied[12c]). The structures of BeH_2 and the anions BeH_3^- and BeH_4^{2-} were also calculated with the small

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