Dihydrogen Bonding in Main Group Elements: A Case Study of Complexes of LiH, BH_3, and AlH_3 with Third-Row Hydrides

Sudhir A. Kulkarni* and Alok Kumar Srivastava

Department of Chemistry, University of Pune, Pune 411 007, India

Received: October 23, 1998; In Final Form: January 25, 1999

A systematic investigation of the occurrence of dihydrogen bonds in the main group elements is taken up. The complexes of LiH, BH_3, and AlH_3 with the third-row hydrides, viz. HCl, H_2S, and PH_3, as well as their dimers are studied at the ab initio MP2 level of theory and compared with the corresponding second-row hydrides. The dihydrogen bonds in the third-row dimers are weaker than those in the second-row ones, with the H···H distance being greater than 2.4 Å in some complexes and dimers. The existence of a bond between such neighboring hydrogens is established on the basis of topographical analysis of electron density. The energy of dihydrogen bonds in the dimers of third-row complexes is similar to the conventional weak H-bonds. The decomposition analysis of interaction energy of dimers shows predominance of an electrostatic component followed by polarization and charge transfer. The present study also suggests reinvestigation of the structure of phosphine−borane (BH_3PH_3) using the IR and NMR techniques.

I. Introduction

It is well known that hydrogen bonding has a profound effect on the nature and properties of compounds.[1] The hydrogen bond (H-bond) acts as glue for building up and designing of molecular crystals.[2] The advantage of H-bonded crystals is that they are weak enough to allow annealing and editing and strong enough to impart stability to the crystal. Considering the versatility of the H-bond, it is of great interest to appraise and compare the newly recognized dihydrogen bond[3] with the conventional H-bonds. Experimentally, such a type of EH···HX (where E is a transition/alkali metal or boron and X is any electronegative atom/group) bond, termed as a dihydrogen bond, has been observed in transition metal complexes. Analogous to the conventional H-bond, both inter- and intramolecular versions of dihydrogen bonds have been observed[4] with H···H distances being less than 2.4 Å (sum of van der Wall (vdW) radii). The existence of dihydrogen bonds in compounds of main group elements has been speculated in the recent years, and ab initio calculations have been used to support this.[5] It is known that hydrides of alkali (group 1) and alkaline earth metals (group 13) have negatively charged hydrogens, which can interact as bases with hydrogens attached to electronegative atoms from groups 15, 16, and 17. An exciting application of dihydrogen bonding has been recently reported[6] in the area of crystal engineering in terms of synthesis of $[(GaH_2NH_2)_3]_2$. The H···H distances have been observed to be in the range of 1.97−2.34 Å from neutron diffraction studies. The theoretical estimates[6] of dimerization energies for various conformers of $[(BH_2NH_2)_3]_2$, $[(AlH_2NH_2)_3]_2$, and $[(GaH_2NH_2)_3]_2$ are in the range 4.1−12.5 kcal/mol. The estimate of H···H bond energy in these structures has been reported to be 3 kcal/mol. The proposition of such stable crystal stems from the existence of stable dimers of BH_3, AlH_3, and GaH_3 with ammonia, viz. $[BH_3NH_3]_2$, $[AlH_3NH_3]_2$ and $[GaH_3NH_3]_2$ as studied by Cramer and Gladfelter.[7] The dimerization energy was shown to decrease from dimers of boron to that of gallium.

Recently, we have investigated[8] dihydrogen-bonded dimers of LiH, BH_3, and AlH_3 with HF, H_2O, and NH_3. Five stable dimer structures were found to exist apart from well studied amine−borane,[5,7] viz. $[H_2OLiH]_2$, $[BH_3HF]_2$, $[BH_3H_2O]_2$, $[AlH_3H_2O]_2$, and $[AlH_3NH_3]_2$. The dimerization energies were found to vary from weak −4.7 kcal/mol for $[BH_3HF]_2$ to a strong ionic −40 kcal/mol for $[H_2OLiH]_2$. The bonding features of these dimers and their monomer complexes were discussed on the basis of topographical properties of electron density. Further, the decomposition analysis of interaction energy for dimers indicated the predominance of electrostatic contribution.

As has been mentioned earlier, the dimer structure forms a basis for the formation of large clusters as well as crystals. Therefore, it is worthwhile to investigate H···H bonded dimers formed by third-row elements. The second-row hydrides such as HF, H_2O, and NH_3 possess significant positive charge on the hydrogen atoms; however, their analogues in the third row have low positive/negative charge. Therefore, a question may be asked of whether H···H bonded dimers are formed by the complexes of LiH, BH_3, and AlH_3 with third-row hydrides of groups 15, 16, and 17. These complexes and dimers are studied and compared with the earlier reports[7,8] on the basis of dimerization energies, bonding features, and contributions of various energy components to interaction energy.

The next section discusses methodology used, whereas discussion on the present results is done in section III. This is followed by topological analysis of electron density distribution and energy decomposition analysis in section IV and concluding remarks in section V.

II. Methodology

The structures of the complexes and their dimers studied herein are obtained using the second-order Moller−Plesset perturbation method (MP2/6-31++G(d,p)) from the program Gaussian 94.[9] The basis set used is of split-valence type including diffuse and polarization functions on hydrogens as well as heavy atoms. The nature of stationary points obtained on the potential energy surface (PES) is confirmed by calculating

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* Corresponding author. E-mail: sakul@chem.unipune.ernet.in.

10.1021/jp984135r CCC: $18.00

TABLE 1: Interaction Energies (kcal/mol) and Dipole Moments, μ (Debye), of Complexes of LiH, BH_3, and AlH_3 with HCl, H_2S, and PH_3 Using 6-31++G(d,p) Basis Set[a]

structure	NIMAG[b]	ΔE(MP2)	ΔE(MP2) + ZPE	ΔE(MP2) + ZPE + BSSE	ΔE(MP4) + ZPE	μ[c]
S_1	1	−9.95	−8.98	−9.05		
S_2	1	−4.55	−3.70	−2.93		
S_3	1	−3.16	−2.31	−1.80		
S_4	0	−11.93	−10.30		−10.41	
S_5	0	−12.66	−10.78			
S_6	0	−23.64	−19.40		−17.95	4.51
S_8	2	−0.66	−0.40	0.03		
S_9	0	−13.28	−8.97		−7.24	4.20
S_{11}	0	−1.13	−0.50	0.01	−0.49	
S_{12}	0	−2.69	−0.87		−0.91	1.73
S_{14}	0	−15.44	−12.77		−12.53	4.42
S_{16}	0	−1.34	−0.32	0.35	−0.33	
S_{17}	0	−12.51	−9.74		−9.71	3.89
S_{19}	0	−5.31	−3.56			
S_{20}	1	−2.25	−1.62	−1.00		

[a] Total energies (in au) of complexing molecules at the MP2 and MP4 levels are: LiH, −8.00284, −8.00876; BH_3, −26.48730, −26.50876; AlH_3, −243.69253, −243.71202; HCl, −460.20776, −460.22639; H_2S, −398.81222, −398.83606; PH_3, −342.58053, −342.60806. [b] Number of imaginary frequencies. [c] Dipole moments calculated at the MP2 level.

TABLE 2: Dimerization Energies (kcal/mol) Including Zero-Point Energies

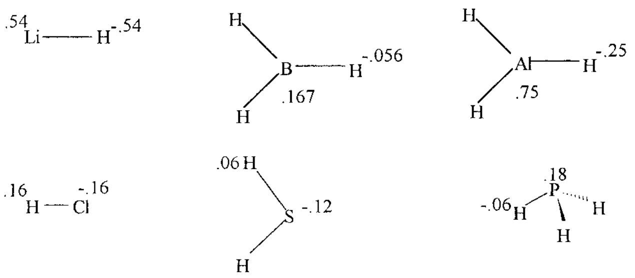
dimer	MP2	MP2+ BSSE	MP2(ex)[a]	MP3	MP4(SDQ)	MP4(SDTQ)
$[BH_3PH_3]_2$	−5.57	−4.35	−5.76	−5.45	−5.30	−5.94
$[BH_3H_2S]_2$	−8.85	−6.67	−8.64	−8.30	−7.99	−6.95
$[BH_3HCl]_2$	−2.63	−3.22	−5.26	−0.93	−0.31	−2.08
$[AlH_3H_2S]_2$	−8.41	−6.96	−8.51	−8.15	−7.79	−7.45
$[AlH_3PH_3]_2$	−5.46	−4.36	−5.92	−5.47	−5.28	−5.79

[a] Dimerization energy using extended basis set (6-311++G(3d,2p)) at the 6-31++G(d,p) geometry.

their vibrational frequencies and estimates of basis set superposition error (BSSE) are obtained at the MP2/6-31++G(d,p) level. The MP2 geometries are used for calculating interaction energies at the fourth-order perturbation method including single, double, triple, and quadruple contributions (MP4(SDTQ)/6-31++G(d,p)) for some complexes and dimers. It is well-known that Mulliken charges are not always adequate to explain bonding in various situations;[10] therefore, molecular electrostatic potential (MEP) derived charges[11] as well as charges from natural population analysis[12] have also been obtained. The topographical analysis of the electron density distribution of all the systems studied here is performed to understand clearly the bonding features of the dihydrogen bonded dimers and their parent complexes (monomers) using the atom in a molecule[13] (AIM) theory from Gaussian 94. The energy decomposition analysis due to Kitaura and Morokuma[14] is performed for dihydrogen-bonded dimers and compared with the corresponding second-row analogues.

III. Results and Discussion

It is known that hydrides of lithium, boron, and aluminum have negatively charged hydrogens, whereas PH_3, H_2S, and HCl possess either low negative or positively charged hydrogens. Simple Mulliken charges of the isolated complexing molecules are given below:



The formation of H···H bonded complexes and dimers may be rationalized using these Mulliken or MEP derived charges. The interaction energies of complexes of LiH, BH_3, and AlH_3 with HCl, H_2S, and PH_3 at the MP2 and MP4 levels of theory are reported in Table 1. The MP2, MP3, and MP4 level dimerization energies of the dihydrogen-bonded dimers are reported in Table 2. In addition, both Tables 1 and 2 report BSSE corrected MP2 energies for H···H bonded complexes and dimers, whereas Table 2 also reports dimerization energies with an extended basis set. The systems EH_nXH_m (where E = Li/B/Al and X = P/S/Cl) are referred to as complexes, whereas $[EH_nXH_m]_2$ are denoted as dimers in the following discussion.

III.A. Complexes of LiH. The H···H bonded complex of LiH with HCl has an almost linear structure (cf. S_1 in Figure 1) with hydrogens 1.413 Å apart and is stabilized by 8.98 kcal/mol. The inclusion of BSSE correction shows similar stabilization (cf. Table 1). However, this complex has one imaginary frequency (197 i) and hence is not discussed further. The complex having a Li−Cl bond does not exist, instead it leads to LiCl + H_2.

Three stationary-point geometries of complexes of LiH with H_2S are found on the PES and shown as S_2−S_4 in Figure 1. Complex S_2 is a monodentate structure with an H···H distance of 1.918 Å and a stabilization of 3.70 kcal/mol. A bidentate structure S_3 has an H···H distance of 2.674 Å and an interaction energy of −2.31 kcal/mol. For both S_2 and S_3, BSSE corrected interaction energies are higher at the MP2 level. In addition, S_2 and S_3 have one imaginary frequency each and hence do not contribute to the structure of the H_2S···LiH complex. Complex S_4 is a minimum on the PES and has a long S···Li bond of 2.513 Å, with stabilization of 10.30 kcal/mol (cf. Table 1). The Mulliken charges of S_4 indicate that there is an enhancement in the negative charge of the hydride of lithium and positive charge of hydrogens attached to sulfur. A dimer formation,

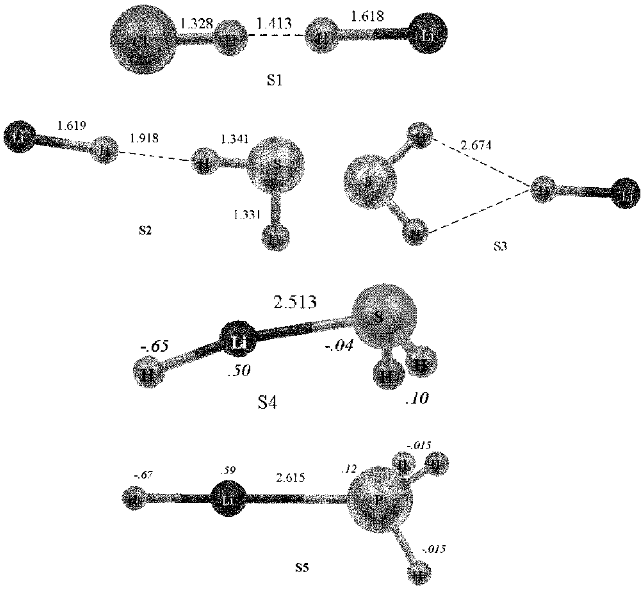


Figure 1. Stationary structures of complexes of LiH with HCl, H_2S, and PH_3. Bond lengths are in angstroms. Mulliken charges are shown in italics for some complexes.

$[H_2SLiH]_2$, in a head to tail manner should be expected from these charges. However, the dihydrogen-bonded dimer is not formed, instead forming a dimer with two LiH···LiH bonds. The difference in Mulliken and MEP-derived charges of H_2S hydrogens and hydride leads to attraction of hydride by lithium of the other complex.

Although PH_3 charges are rather different from NH_3, a P···Li bonded (distance of 2.615 Å) complex of PH_3···LiH is found to be stabilized by 10.78 kcal/mol (see S_5 in Figure 1). The dimer of this complex forms a structure analogous to $[NH_3LiH]_2$, without a H···H bond.[8] This may also be explained on the basis of the difference of charges on hydrogens attached to Li and P, respectively. The dimers $[PH_3LiH]_2$ and $[H_2SLiH]_2$ which do not exhibit H···H bonding are not shown in Figure 1 due to paucity of space.

LiH does not form stable dihydrogen-bonded complexes or the corresponding dimers with third-row hydrides. In the case of second-row hydrides,[8] LiH forms a complex with H_2O having a H···H bond and the most stable dihydrogen bond was found in $[H_2OLiH]_2$.

III.B. Complexes of BH_3. The structure of phosphine−borane, BH_3PH_3, has been investigated using high-resolution NMR, infrared, and Raman spectroscopy and was proposed to exist in monomeric form[12] in the liquid as well as the solid state. However, it was indicated about 30 years ago that BH_3PH_3 may exist with P−H···H−B bonding.[15] It should be noted that BH_3PH_3 exists in the molten state at 37 °C, whereas isoelectronic propane and ethanol have their melting points of −189.7 °C and −117.3 °C, respectively. In view of this, the H···H bonded dimer of the complex should be investigated.

The complex BH_3···PH_3 (cf. S_6 in Figure 2) has a B···P bond of 1.947 Å. This complex is a minimum on the PES with an interaction energy of −17.95 kcal/mol (cf. Table 1). The PH_3 hydrogens become weakly positive after complexation; however, the negative charge on the hydrogens of BH_3 is reduced. The MEP-driven as well as natural charges show negative charge on hydrogens attached to B as well as P. Thus, the situation is not favorable for the H···H bonded dimer formation. An attempt to obtain a structure for dimer $[BH_3PH_3]_2$ shows formation of two bidentate dihydrogen bonds of length 2.57 and 2.69 Å, respectively, as shown in S_7 in Figure 2. The H···H distance in the dimer clearly exceeds the sum of vdW radii (2.4 Å) and the B−P bond in the dimer has elongated by 0.005 Å. This is in sharp contrast with other H···H bonded dimers, wherein the dimer shows shorter E−X bonds compared to the corresponding monomer.[8] Although the H···H bonds are too long, Table 2 shows a dimerization energy of −5.57 and −5.94 kcal/mol at the MP2 and MP4 levels, respectively. The use of an extended basis set does not alter the result, whereas the inclusion of BSSE correction reduces the dimerization energy (cf. Table 2). This indicates a bond energy of about 1.1−1.5 kcal/mol to every H···H bond, if bonding is bidentate as shown in S_7 of Figure 2. Such weak bonds may not have significant effects on the IR and NMR spectra of this system, leading to the conclusion that BH_3PH_3 exists in monomeric form. However, the formation of the dihydrogen-bonded dimer, $[BH_3PH_3]_2$, may result in the higher melting temperature of phosphine−borane compared to isoelectronic propane and ethanol. These facts along with the above dimer structure suggest the necessity of structural reinvestigation of BH_3PH_3 using the current advanced experimental techniques.

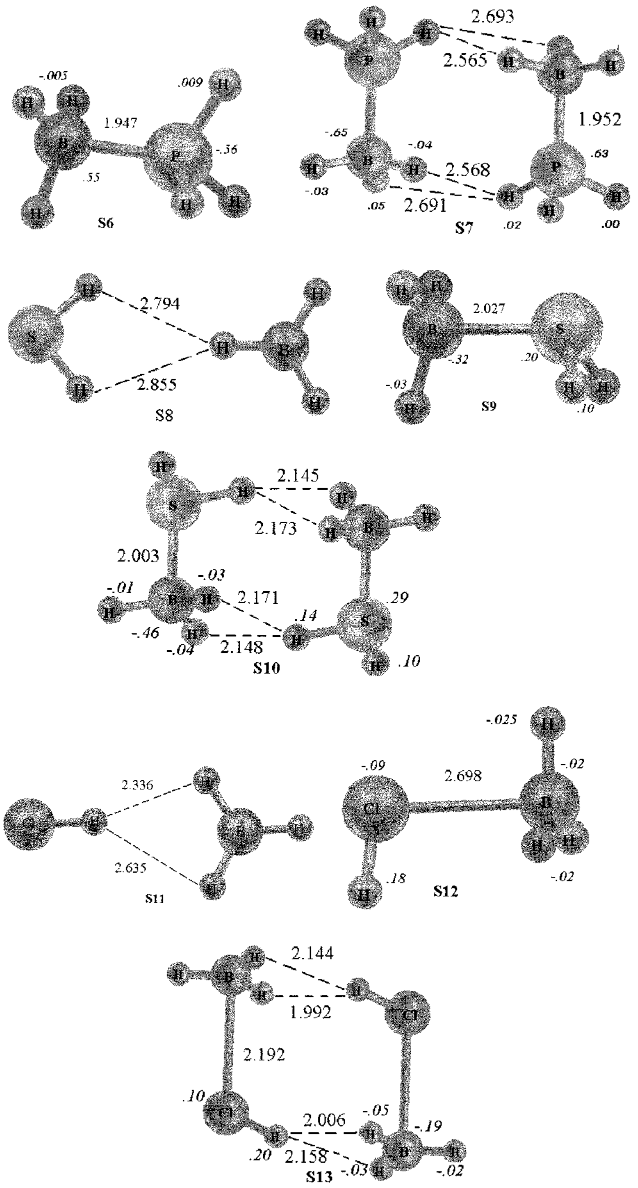


Figure 2. Stationary structures of complexes of BH_3 with HCl, H_2S and PH_3 and dimers of complexes. Bond lengths are in angstroms. The Mulliken charges are shown in italics for some complexes.

The complexes of BH_3 with H_2S (S_8 in Figure 2) possess a bidentate structure involving one of the hydrogens of BH_3 with two of H_2S. The H···H bond in this structure is more than 2.4 Å and hence has meager stabilization or is destabilized after inclusion of BSSE correction. A complex involving a B···S bond (S_9) of 2.027 Å is a minimum on the PES having an interaction energy of −7.24 kcal/mol. The positive charge on H_2S hydrogens increased further on complexation, while the negative charge on the BH_3 hydrogens has decreased, thereby favoring the formation of the dimer, $[BH_3H_2S]_2$.

The dimer $[BH_3H_2S]_2$ also has a structure wherein one of the hydrogens of H_2S is involved in a bidentate dihydrogen bonding resulting in a cagelike structure (S_{10}). The H···H bond distances of the bidentate bonding are 2.146 and 2.172 Å. The B−S bond distance in the dimer is 2.003 Å, which is shorter than the corresponding distance in the monomer (BH_3H_2S) by 0.024 Å. The dimerization energy of the $[BH_3H_2S]_2$ is −8.85 and −6.95 kcal/mol at the MP2 and MP4 levels, respectively. The BSSE corrected dimerization energy is similar to the corresponding MP4 one (cf. Table 2).

Two complexes of BH_3 with HCl exist on the PES (cf. S_{11} and S_{12}). One complex is an asymmetric bidentate H···H bonded structure (S_{11}) which is a minimum on the PES with a stabilization of −0.50 kcal/mol at the MP2 level. However, this complex is not stabilized after the inclusion of BSSE correction. The other complex is weakly bound B···Cl bonded (S_{12}) with a distance of 2.698 Å and a H−B−Cl−H dihedral of 0°. This complex has an interaction energy of −0.91 kcal/mol at the MP4 level.

The dimer of BH_3HCl also has the hydrogen of HCl involved in a bidentate dihydrogen bonding resulting in the formation of a cagelike structure (S_{13}). The H···H bond distances of one of the bidentate dihydrogen bonding sites in S_{13} are 1.992 and 2.144 Å. The corresponding distances for the other bidentate dihydrogen bonding in S_{13} are 2.006 and 2.158 Å. The B−Cl bond distance in $[BH_3HCl]_2$ is 2.192 Å, which is 0.506 Å shorter than the corresponding distance in the monomer. The dimerization energy of the $[BH_3HCl]_2$ is −2.63 and −2.08 kcal/mol at the MP2 and MP4 levels, respectively. Due to large deformations in monomer geometry in the dimer, the BSSE correction shows more stabilization for this dimer (cf. Table 2). Such small dimerization energy may be a result of a long H···H bond and an increase in steric interaction due to a short B−Cl bond in the dimer.

A comparison of the dimers of BH_3 with PH_3, H_2S, and HCl indicates that the H···H bond becomes short and strong for $[BH_3HCl]_2$ followed by $[BH_3H_2S]_2$ and $[BH_3PH_3]_2$. However, the strength of the H···H bond is not directly related to the dimerization energies, as there are more relaxation effects involved in the dimer formation.

III.C. Complexes of AlH_3. The complex of AlH_3 with PH_3 (S_{14}) has an Al···P bond distance of 2.555 Å, and its interaction energy is −12.77 kcal/mol (cf. Table 1). These are comparable to the corresponding CCSD level structure[16] using DZP basis. The Mulliken charges of the complex show that the hydrogens of PH_3 have become positively charged (the isolated PH_3 shows small negative charge on the hydrogens), while the charges on the hydrogens of AlH_3 are unaltered. This hints at the possible dimer formation of AlH_3PH_3. Calculation for other H···H bonded complexes yielded no structure with significant stabilization energy.

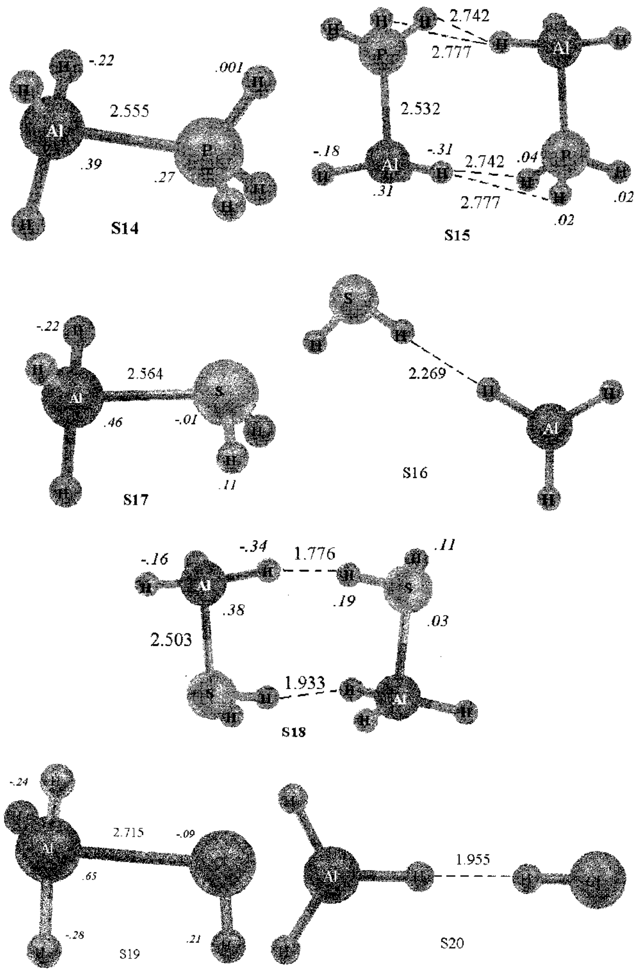


Figure 3. Stationary structures of complexes of AlH_3 with HCl, H_2S, and PH_3 and dimers of complexes. Bond lengths are in angstroms. The Mulliken charges are shown in italics for some complexes.

The dimer of AlH_3PH_3 consists of two bidentate dihydrogen bonds in which one of the hydrogens of AlH_3 is bonded to two hydrogens of PH_3 (S_{15}), the H···H distances being 2.777 and 2.742 Å. This type of bonding results in a complex cagelike structure. The Al−P bond distance is 2.532 Å in the dimer, $[AlH_3PH_3]_2$, which is 0.022 Å shorter than in the monomer (cf. S_{14} and S_{15} in Figure 3). The dimerization energy of the $[AlH_3PH_3]_2$ is −5.46 and −5.79 kcal/mol at the MP2 and MP4 levels, respectively. Thus, analogous to $[BH_3PH_3]_2$, the H···H distance for $[AlH_3PH_3]_2$ is greater than 2.4 Å and each H···H bond has an energy of about 1.4 kcal/mol considering their bifurcated nature. The dimerization energy gets reduced after the BSSE correction, whereas it does not alter significantly due to use of the extended basis set.

The complex of AlH_3 with H_2S (S_{16}) involves a monodentate H···H bond of 2.269 Å and an interaction energy of −0.32 kcal/mol. Although this complex is a minimum on the PES, it is not stabilized after the inclusion of BSSE correction (cf. Table 1). Yet another structure of the same complex (S_{17}) involving Al···S bonding has a bond distance of 2.564 Å and an interaction energy of −9.74 kcal/mol. The Mulliken charges of the complex show that the hydrides of Al have small reduction in their negative charge while the hydrogens of H_2S become more positively charged, indicating possible formation AlH_3H_2S dimer.

The dimer of AlH_3H_2S develops an eight-membered structure wherein two dihydrogen bonds of different length are formed (S_{18}). The two H···H bond distances are different, 1.933 and 1.776 Å. The Al−S bond distance in the dimer, $[AlH_3H_2S]_2$, is 2.505 Å, which is 0.05 Å shorter than the Al−S distance in the monomer (cf. S_{17} and S_{18} in Figure 3). The dimerization energy of $[AlH_3H_2S]_2$ is -8.41 and -7.45 kcal/mol at the MP2 and MP4 levels, whereas it is -6.96 kcal/mol with BSSE correction (cf. Table 2). In comparison to $[BH_3H_2S]_2$, the H···H bond distance in $[AlH_3H_2S]_2$ is smaller due to higher negative charge on AlH_3 hydrogens. As the hydrogens of H_2S bear weaker positive charge compared to H_2O, the H···H distance in the present dimer is larger by about 0.2−0.4 Å compared to $[AlH_3H_2O]_2$.

The complex of AlH_3 with HCl (S_{19}) has a Al···Cl bond distance of 2.715 Å and a H−Cl−Al−H dihedral of 3.2° with an H···H distance of 2.881 Å. This complex is a minimum on the PES with an interaction energy of -3.56 kcal/mol. The Al···Cl distance is shorter with more stabilization energy of 0.45 kcal/mol for S_{19} compared to the earlier reports of Hartree−Fock level geometries and the MP4 level energetics.[17] The complex (S_{20}) of AlH_3 with HCl involving a monodentate H···H bond of 1.955 Å distance has one imaginary frequency of 12i. A stable H···H bonded dimer of AlH_3HCl is not observed, which instead forms $AlH_2Cl + H_2$. This case is similar to that of the AlH_3HF dimer wherein $AlH_2F + H_2$ are formed.[8] This may be attributed to hydrogen charges of almost equal magnitude attached to Al and Cl, respectively, or to the intramolecular H···H bond which becomes stronger leading to elimination of H_2.

To verify that the MP2 level calculations are indeed sufficient for H···H bonded complexes, viz. S_1, S_2, S_8, S_{11}, S_{16} and S_{20}, we have obtained optimized structures and vibrational frequencies at the MP4(SDQ)/6-31++G(d,p) level. The interaction energies are similar to their MP2 counterparts and the nature of stationary points remains unchanged by the addition of a higher level of correlation. Further, the dimerization energies are also computed at the MP2/6-311++G(3d,2p) level using the MP2/6-31++G(d,p) geometries. The use of an extended basis set has no major effects on trends in the dimerization energies of third-row dimers (cf. Table 2), except in the case of $[BH_3HCl]_2$, which is further stabilized by about 2 times than the corresponding lower basis set.

The incorporation of correction due to basis set superposition error (BSSE) is normally considered to be vital in the weakly bonded as well as hydrogen bonded complexes.[18] However, there are several conflicting reports on the validity of results after inclusion of BSSE correction.[19] We have included the BSSE corrected energies for some H···H bonded complexes and dimers in Tables 1 and 2 by employing the counterpoise method.[20] In general, the H···H bonded complexes as well as dimers are less stabilized after correction for BSSE and the complexes S_8, S_{11}, and S_{16} are found to be destabilized. In case of H···H bonded dimers, the trends in dimerization energies do not change even after inclusion of BSSE correction. The dimer $[BH_3HCl]_2$ gets more stabilized due to large monomer geometry deformations in the dimer.

Some similarities and differences in the complexes as well as dimers of LiH, BH_3, and AlH_3 with second- and third-row hydrides should be noted. The $[BH_3HCl]_2$ has the least H···H bond energy and has a significantly shorter B−Cl bond in the dimer than in the monomer, which is similar to $[BH_3HF]_2$ in the second-row dimers. The E−X bond (E, metal; X, heteroatom) in the dimers of second-row hydrides is significantly shorter than the monomers of the corresponding third-row hydrides. The dimerization energies are in the order $[AlH_3H_2S]_2 > [BH_3H_2S]_2 > [BH_3PH_3]_2 > [AlH_3PH_3]_2 > [BH_3HCl]_2$ which is similar to that found in the corresponding second-row hydrides.[8] The dimerization energy of complexes of BH_3 with second-row hydrides is about 1.75 times that with the corresponding third-row hydrides, whereas it is 2.1 times for the complexes of AlH_3. The trends observed in H···H bond distance in the dimers of second-row hydrides are also maintained in the dimers of third-row hydrides. The H···H distances are much longer in the third-row hydrides than the second-row ones. For second-row H···H bonded dimers, the dimerization energies follow the same order as exhibited by the dipole moments of their monomers; such trends are not observed for the corresponding third-row dimers.

It should be noted that the complexes of LiH, BH_3, and AlH_3 with PH_3, H_2S, and HCl and their dimers show a variety of bonding features. Some complexes with H···H bonding are also found to be minima on their PES. Further, for some dimers, the H···H bonds are bifurcated and distances are found to be longer than 2.4 Å with reasonable stabilization. In view of this, the following questions may be raised: whether the ED distributions shows features corresponding to a bond between H···H for bonds longer than 2.4 Å; whether there exists bifuracated bonding in several dimers studied here? These questions along with other bonding features are investigated using their electron density analysis presented in the next section.

IV. Electron Density and Energy Decomposition Analysis

The bonding patterns of dihydrogen-bonded dimers can be reliably obtained from detailed analysis of electron density (ED) via its topographical study. In this analysis, critical points (points for which $\nabla\rho(\mathbf{r}) = 0$) of ED distribution are obtained and further characterization is done using the corresponding Hessian matrix[13] (a matrix of second-order partial derivatives). The existence of a critical point (CP) of (3,−1) type between two nuclei is a signature of bond and the corresponding CP is called as bond critical point (BCP). The ED, its Laplacian and bond ellipticity (defined from eigenvalues λ_i's of the Hessian matrix as $\epsilon = \lambda_1/\lambda_2 - 1$ with $|\lambda_1| > |\lambda_2|$) parameters have been used in the present analysis (cf. Table 3). The negative Laplacian is an indicator of a covalent bond, whereas a positive Laplacian indicates noncovalent interaction.[21] The bond ellipticity is a measure of stability, and higher values indicate instability in the bond.[22]

Among the complexing molecules, the Al−H bond in AlH_3 and P−H bond in PH_3 have low electron densities with positive Laplacian. Even after complexation or dimerization, the Laplacian remains positive for these bonds (cf. Table 3). In the case of AlH_3H_2S, the Al−S bond has low ED and low positive Laplacian indicating noncovalent interaction. The Al−S bond becomes stronger, whereas the Al−H bond involved in H···H bonding becomes weaker in case of $[AlH_3H_2S]_2$ compared to its monomer. The BCP for the dihydrogen bond shows a positive Laplacian indicating weaker and closed-shell interaction. The H···H bonds in $[AlH_3H_2S]_2$ are the strongest among other dimers and are more stable, as can be inferred from their least ellipticities. On the other hand, for BH_3H_2S, the B−S bond is weak with high ellipticity. The B−S bond in the dimer is shorter with a higher ED value for its bond CP and has reduced ellipticity indicating the existence of a more stable B−S bond in the dimer compared to the monomer. One more surprising feature of $[BH_3H_2S]_2$ is that, instead of an H···H bond it shows a bond between (S)−H···B with a very large ellipticity. This may be an artifact of the electropositive hydrogen being shared by two electronegative hydrogens attached to boron, the bifurcation of bond paths from this BCP might lead to such an ED structure. Although for $[BH_3PH_3]_2$ and $[AlH_3PH_3]_2$ the H···H bond is longer than 2.4 Å, they show CP corresponding

TABLE 3: Electron Density Critical Points (CP) and Laplacian of Electron Density and Bond Ellipticity (ϵ) of Complexing Molecules, Complexes, and Dimers at MP2/6-31++G(d,p) Geometry

molecule	location of CP	type of CP	$\rho(r)$	$\nabla^2\rho(r)$	ϵ
AlH_3	Al−H bond	(3,−1)	0.080	0.292	0.02
H_2S	S−H bond	(3,−1)	0.222	−0.609	
AlH_3H_2S	Al−H bond	(3,−1)	0.078	0.287	0.02
	Al−S bond	(3,−1)	0.027	0.099	0.04
	S−H bond	(3,−1)	0.226	−0.707	0.15
	Al−H′ bond	(3,−1)	0.078	0.287	0.02
$[AlH_3H_2S]_2$	Al−H bond	(3,−1)	0.079	0.278	0.02
	Al−H′ bond	(3,−1)	0.073	0.290	0.02
	Al−S bond	(3,−1)	0.032	0.116	0.04
	S−H bond	(3,−1)	0.226	−0.707	0.09
	H⋯H bond	(3,−1)	0.019	0.038	0.02
	S′−H bond	(3,−1)	0.225	−0.701	0.09
	Al′−S bond	(3,−1)	0.033	0.119	0.03
	H⋯H bond	(3,−1)	0.016	0.035	0.09
	Al′−H bond	(3,−1)	0.079	0.280	0.10
	Al′−H bond	(3,−1)	0.077	0.291	0.16
	Al′−H bond	(3,−1)	0.074	0.285	0.12
PH_3	P−H bond	(3,−1)	0.163	0.085	
AlH_3PH_3	Al−H bond	(3,−1)	0.077	0.284	0.02
	Al−P bond	(3,−1)	0.033	0.106	0.00
	P−H bond	(3,−1)	0.169	0.078	0.09
$[AlH_3PH_3]_2$	P−H bond	(3,−1)	0.172	0.071	0.09
	P−H′ bond	(3,−1)	0.169	0.083	0.09
	P−H″ bond	(3,−1)	0.171	0.073	0.09
	P−Al bond	(3,−1)	0.036	0.111	0.04
	Al−H bond	(3,−1)	0.076	0.282	0.02
	Al−H′ bond	(3,−1)	0.077	0.286	0.02
	Al−H″ bond	(3,−1)	0.076	0.285	0.01
	H⋯H bond	(3,−1)	0.007	0.021	0.78
BH_3	B−H bond	(3,−1)	0.185	−0.226	
BH_3H_2S	S−H bond	(3,−1)	0.228	−0.728	0.12
	B−S bond	(3,−1)	0.073	0.227	0.53
	B−H bond	(3,−1)	0.172	−0.108	0.17
	B−H′ bond	(3,−1)	0.171	−0.103	0.17
$[BH_3H_2S]_2$	S−H bond	(3,−1)	0.225	−0.679	0.07
	S−H′ bond	(3,−1)	0.223	−0.666	0.08
	B−S bond	(3,−1)	0.084	0.126	0.1
	B−H bond	(3,−1)	0.169	−0.130	0.15
	B−H′ bond	(3,−1)	0.172	−0.160	0.14
	B−H″ bond	(3,−1)	0.168	−0.130	0.16
	H⋯H bond	(3,−1)	0.012	0.036	3.61
	ring CP	(3,+1)	0.003		
HCl	H−Cl bond	(3,−1)	0.578	−3.504	
BH_3HCl	H−Cl bond	(3,−1)	0.260	−0.904	0.00
	B−H bond	(3,−1)	0.183	−0.207	0.30
$[BH_3HCl]_2$	H−Cl bond	(3,−1)	0.251	−0.874	0.02
	B−H bond	(3,−1)	0.178	−0.200	0.26
	B−H′ bond	(3,−1)	0.181	−0.231	0.23
	B−H″ bond	(3,−1)	0.175	−0.185	0.27
	H⋯H bond	(3,−1)	0.014	0.039	1.49
BH_3PH_3	B−H bond	(3,−1)	0.165	−0.062	0.08
	B−P bond	(3,−1)	0.101	0.192	0.00
	P−H bond	(3,−1)	0.171	0.080	0.05
$[BH_3PH_3]_2$	B−H bond	(3,−1)	0.164	−0.033	0.08
	B−H′ bond	(3,−1)	0.166	−0.064	0.07
	B−P bond	(3,−1)	0.103	0.159	0.04
	P−H bond	(3,−1)	0.173	0.077	0.05
	P−H′ bond	(3,−1)	0.171	0.085	0.05
	P−H″ bond	(3,−1)	0.175	0.071	0.05
	H⋯H bond	(3,−1)	0.007	0.024	1.69

to dihydrogen bonds. However, such CP exists only between the shorter of the two bidentate H⋯H bonds for all the dimers shown in Figures 2 and 3, except the $[BH_3H_2S]_2$. The ED values of these H⋯H bonds are low with large ellipticities, indicating that these bonds are prone to dissociate (see Table 3).

Table 4 displays the results of decomposition of interaction energy for some dimers into various components such as electrostatic (ES), exchange (EX), polarization (PL), and charge transfer (CT), using the Kitaura and Morokuma[14] scheme. The analysis carried out for some dimers at their MP2 geometries shows predominance of the electrostatic component followed by polarization and charge transfer. The dimers of second-row elements exhibit the order ES > CT > PL.

TABLE 4: Energy Decomposition Analysis[a] of Interaction Energies of Dihydrogen Bonded Dimers[b]

molecule (structure)	ES	EX	PL	CT	mix	total
$[BH_3H_2S]_2$ (S_{10})	−12.29	11.36	−4.95	−3.59	3.94	−5.53
$[BH_3PH_3]_2$ (S_7)	−8.14	6.73	−3.54	−1.52	2.99	−3.49
$[AlH_3PH_3]_2$ (S_{15})	−9.08	7.67	−4.80	−2.18	4.45	−3.94

[a] For details of energy decomposition analysis see ref 14. The MP2 optimized geometries are used for the analysis. [b] All values are in kcal/mol.

V. Concluding Remarks

The occurrence of dihydrogen bonds in the complexes and dimers of complexes of LiH, BH_3, and AlH_3 with HCl, H_2S, and PH_3 is systematically investigated at the ab initio MP2 level of theory. The H⋯H bonding herein is compared with the complexes of LiH, BH_3, and AlH_3 with HF, H_2O, and NH_3. Most of the H⋯H bonded complexes of the third-row hydrides are not minima on their PES, and those which are minima have meager stabilization. The optimization and calculation of frequencies at the MP4(SDQ) level for H⋯H bonded complexes indicate that the nature of the stationary point remains the same as that at the MP2 level and interaction energies are comparable. However, the inclusion of BSSE correction in general reduces the relative stabilization of the H⋯H bonded complexes. On the other hand, the H⋯H bonded dimers show low to moderate stabilization with or without inclusion of BSSE and using the extended basis set. The formation of complexes and their dimers is explained on the basis of the atomic charges, and Mulliken charges are found to be adequate for this purpose. The Mulliken charges seem to be consistent with natural charges in most of the cases, whereas MEP derived charges are different for a few cases, although the overall predictions do not change. The ED topographical analysis of the dimers shows the existence of an H⋯H bond between the shorter of the two hydrogens in bifurcated configuration. Thus, a short H⋯H distance does not necessarily correspond to the existence of a bond between two atoms. Moreover, there exists a weak bond between H⋯H despite the distance being greater that 2.4 Å. This clearly indicates that each H⋯H bond has an energy of about 3 kcal/mol for the dimers involving third-row hydrides (with an exception of $[BH_3HCl]_2$). The bifurcated bonding has been observed only for $[BH_3H_2S]_2$. Considering the stability of $[BH_3PH_3]_2$, its structural reinvestigation using recent experimental techniques seems to be worthwhile. The energy of hydrogen bonds involving Cl−H, S−H, and P−H bonds is known to be in the range of moderate to weak H-bonds.[18] The energy of dihydrogen bonds in the dimers of third-row complexes is also similar to conventional weak H-bonds. In contrast with the second-row complexes in which dimerization energies follow trends similar to the dipole moments of monomer complexes, the corresponding third-row dimers show no such trends. The decomposition analysis of interaction energy shows that H⋯H bonding in this case is predominantly electrostatic with the polarization term being more dominant than the charge transfer.

Comparison with our previous work[8] clearly indicates that although the dihydrogen bonding in the dimers of third-row elements is weaker, it still satisfies criteria of forming stable crystals mentioned in the Introduction. This opens up new avenues in crystal engineering wherein the dihydrogen bonds may act as glue for formation and stability of the crystal.

Acknowledgment. The authors are thankful for financial assistance from University Grants Commission in the form of a minor research grant. We are grateful to Professor S. R. Gadre for his help at every stage of this work.

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