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Competition between Nonclassical Hydrogen-Bonded Acceptor Sites in Complexes of Neutral AH_2 Radicals (A = B, Al, and Ga): A Theoretical Investigation

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An ab initio computational study of the properties of the neutral AH_2 radicals (A = B, Al, Ga) as hydrogen-bond (HB) acceptors, with H−X (X = F, Cl, Br, CN, and CCH) as HB donors, is carried out at the UMP2/6-311++G(2d,2p) level. Two different minima have been found for each of the 15 possible dimers. One structure corresponds to a single-electron hydrogen-bonded complex (SEHB), with the A atom acting as an HB acceptor. The second corresponds to a dihydrogen bond complex between one of the hydrogen atoms of AH_2 and the H−X molecule. Thus, all the atoms of the neutral AH_2 molecule can act as HB acceptors and none as donors. The stability of the SEHB complexes decreases as $BH_2 > AlH_2 > GaH_2$, while for the dihydrogen-bonded complexes the order is $AlH_2 > GaH_2 > BH_2$. For the BH_2 radical the SEHB complexes are stronger than the dihydrogen bonded ones, while the opposite is found for the AlH_2 and GaH_2 systems. Regarding the HB donors, the order found for the binding energy in the two types of complexes is $H_2A\cdots HF > H_2A\cdots HCl > H_2A\cdots HBr > H_2A\cdots HCN > H_2A\cdots HCCH$.

1. Introduction

Since the beginning of the 20th century, hydrogen bonds (HB) have attracted much attention[1−3] because of their important roles in chemistry, physics, and biology. A HB can be defined as an intermolecular attraction between a hydrogen atom with a partial positive charge and an electronegative region in the acceptor moiety. A conventional hydrogen bond occurs when the electron-deficient hydrogen is attracted to the localized lone pairs on an electronegative atom. In recent years the list of moieties that can act as HB donor and acceptors has greatly expanded.[4,5]

One of the new HB possibilities corresponds to that where the electron donor is a radical and participates in the HB via a single electron. It has been shown that the unpaired electron of the methyl radical may attract the hydrogen atom of a proton donor, forming a kind of unconventional HB called single-electron hydrogen bond (SEHB).[6,7] Some of us have examined the ability of hydrocarbon radicals as HB acceptors[8] and shown that the carbon radicals are poor HB acceptors. It was pointed out, from the electron density topological point of view (atoms in molecules[9]), that the HB complexes involving radicals behave differently from other HBs formed between neutral molecules. Nevertheless, it is worth noting that the HBs formed from radicals exhibit the same spectroscopic properties as the classical HBs ($A\cdots H-B$): a lengthening of the H−B distance[10] and a red-shift of the H−B vibrational frequency[11] in going from free H−B to the HB complex. Recently, the experimental study of the $H_3C\cdots HCN$ complex has been carried out using infrared laser spectroscopy.[12]

A combination of SEHB and dihydrogen bond (DHB)[13] is present in the $(FH)_2\{e\}(HF)_2$ complex,[14] where the loosely bound (excess) electron can form a bridge connecting hydrogen fluoride dimers and can additionally act as an acceptor of the two hydrogen atoms.

To the best of our knowledge, there is no theoretical or experimental report available in the literature concerning SEHB complexes between radicals of electropositive atoms and hydrogen bond donors. In the absence of an experimental search for the single-electron HBs of title radicals, a theoretical analysis of their properties would appear to be in order. Therefore, the present work reports a detailed examination of the stabilities, electronic structure, and vibrational frequencies of the complexes formed between these radicals with H−X (X = F, Cl, Br, CN, and CCH) molecules.

2. Computational Details

Calculations were performed using the Gaussian03 program.[15] Geometry optimizations and frequency calculations were performed at the UMP2 level[16] using the 6-311++G(2d,2p) basis set.[17] Harmonic vibrational frequency calculations were performed, to confirm that the obtained structures were local minima in the potential energy surfaces (PESs) of the studied complexes. The charge distribution has been analyzed by the natural bond orbital (NBO)[18] partitioning scheme at the UMP2/6-311++G(2d,2p) level. The counterpoise (CP) method[19] was used to correct the basis set superposition error (BSSE) in the calculation of the binding energy.

3. Results and Discussion

Single Electron Hydrogen-Bonded (SEHB) Complexes. Two different configurations have been explored for the possible complexes between the AH_2 radical (A = B, Al, and Ga) and H−X (X = F, Cl, Br, CN, and CCH), as shown in Figure 1. The first configuration corresponds to a SEHB where the H−X

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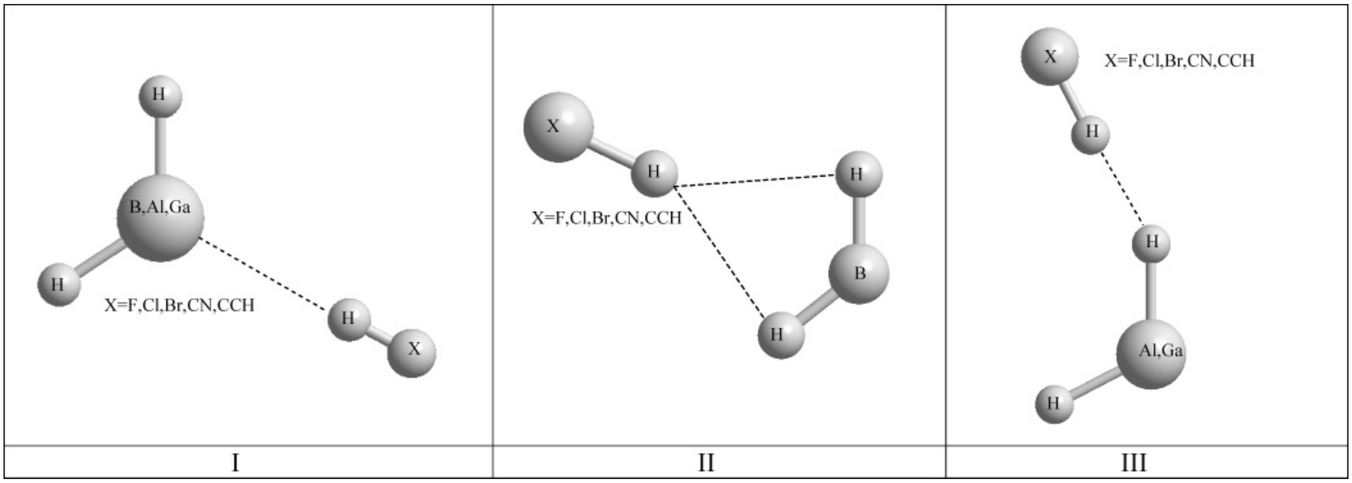

Figure 1. General scheme of single-electron hydrogen-bonded and dihydrogen-bonded complexes considered in the study.

TABLE 1: Binding Energies, Frequency Shift, Charge Transfer, Dipole Moment, and Electronic Interpenetration of the Complexes of AH_2 (A = B, Al, and Ga) Radicals with H−X (X = F, Cl, Br, HCN, and CCH) in Configuration I at the UMP2/6-311++G(2d,2p) Level

complex	ΔE (kJ/mol)	BSSE (kJ/mol)	$\Delta E^{cp\,a}$ (kJ/mol)	$\nu_{int}{}^{b}$ (cm^{-1})	$\Delta\nu_{H-X(C)}$ (cm^{-1})	q^{c} (me)	$R_{A\cdots H}$ (Å)	$\Delta r_{H-X(c)}$ (mÅ)	Q^{d} (me)	μ (D)	interpenetration (Å)	dipole moment enhancement (D)
$BH_2\cdots HF$	−16.3	2.2	−14.1	136	−260	36	2.278	11	3.6	3.058	1.101	0.70
$BH_2\cdots HCl$	−11.9	2.6	−9.3	94	−270	67	2.329	17	4.1	2.332	1.182	0.67
$BH_2\cdots HBr$	−10.6	2.3	−8.3	45	−444	160	2.164	31	7.8	2.364	1.382	0.96
$BH_2\cdots HCN$	−7.8	1.0	−6.8	80	−44	11	2.865	3	17.1	4.194	0.635	0.69
$BH_2\cdots HCCH$	−4.5	0.9	−3.6	63	−12	5	3.026	2	0.2	0.708	0.501	0.23
$AlH_2\cdots HF$	−9.8	1.6	−8.2	82	−177	18	2.889	7	1.6	2.317	0.828	0.98
$AlH_2\cdots HCl$	−7.0	1.7	−5.3	56	−155	26	2.996	10	1.9	1.393	0.853	0.75
$AlH_2\cdots HBr$	−6.2	1.2	−5.0	44	−164	38	2.983	11	1.8	1.184	0.901	0.80
$AlH_2\cdots HCN$	−4.2	0.9	−3.3	47	−27	7	3.534	2	19.0	3.380	0.304	0.90
$AlH_2\cdots HCCH$	−2.9	0.6	−2.3	38	−8	3	3.673	1	0.13	0.232	0.192	0.31
$GaH_2\cdots HF$	−9.7	2.1	−7.7	71	−184	61	2.803	8	2.03	2.471	0.880	0.92
$GaH_2\cdots HCl$	−7.0	2.0	−5.0	44	−157	25	2.926	10	2.2	1.521	0.889	0.66
$GaH_2\cdots HBr$	−6.4	1.6	−4.8	31	−160	32	2.931	11	2.08	1.305	0.919	0.70
$GaH_2\cdots HCN$	−4.4	1.1	−3.3	40	−26	7	3.476	2	15.6	3.517	0.328	0.82
$GaH_2\cdots HCCH$	−3.0	1.1	−1.9	33	−8	2	3.594	1	0.22	0.095	0.237	0.23

[a] ΔE^{cp} refers to binding energy after BSSE correction. [b] ν_{int} refers to intermolecular stretching frequencies. [c] Charge transferred (A→ σ^* H−X(C)) in me. [d] Total charge transferred in me.

molecules point toward the A atom of AH_2, forming C_{2v} complexes. These structures were calculated to be minima at the UMP2/6-311++G(2d,2p) level of theory. It is worth mentioning that the electronic analysis of the isolated AH_2 radicals shows that the spin density is mostly centered on the A atom (1.02, 0.85, and 0.77 for the BH_2, AlH_2, and GaH_2 molecules, respectively) and that this atom is positively charged in the Mulliken population analysis (0.13, 0.57, and 0.55 e, respectively) and NBO analysis (0.67, 0.89, and 0.81 e). The most important results of the mentioned complexes are gathered in Table 1.

The computed binding energies of the $H_2A\cdots HX$ SEHB complexes, reported in Table 1, vary between −14.11 kJ/mol for the $H_2B\cdots HF$ complex to −1.90 kJ/mol for $H_2Ga\cdots HCCH$. For comparative purposes, the corrected binding energies described for the $H_3C\cdots HF$ and $H_3C\cdots HCN$ complexes are −8.50 and −4.77 kJ/mol, respectively.[7] These binding energies are lower than those obtained for the BH_2 complexes and of the same magnitude as those of AlH_2 and GaH_2. Regarding the HB acceptor molecule, the strongest complexes for a given HB donor are obtained with BH_2, followed by AlH_2; those of GaH_2 are slightly weaker. With respect to the HB donor molecules, the stability of the complexes is ordered as follows: $H_2A\cdots HF > H_2A\cdots HCl > H_2A\cdots HBr > H_2A\cdots HCN > H_2A\cdots HCCH$.

The interatomic distances range between 2.164 Å for $H_2B\cdots HBr$ and 3.673 Å for $H_2Al\cdots HCCH$. In general, there is a relation between the interatomic distance and the binding energy. Nevertheless, the dispersion is important as well. Interestingly, the interatomic distance of the GaH_2 complex is shorter than in the corresponding AlH_2 complex. To evaluate the extent of overlap of the electronic clouds of donors and acceptors, the distance at which the electron density 0.001 e isosurface has been determined in the isolated monomers, in the direction where the HB will approach. The calculated radii of isolated AlH_2 and GaH_2 are 2.61 and 2.58 Å, respectively, in agreement with the HB distances in the corresponding complexes.

The difference between the interatomic distance within each complex, and the sum of the values obtained for the corresponding donor and acceptor 0.001 e isosurface in the HB direction, ranges between 1.38 Å for $H_2B\cdots HBr$ and 0.19 Å for $H_2Al\cdots HCCH$. The mutual penetration of the electronic clouds has been defined as a necessary condition for formation of HB interactions.[10] Independently considering the complexes of each HB donor, a linear correlation is found between the binding energy and the total interpenetration of the electronic clouds for each case (the square correlation coefficient is larger than 0.99 for the five HB donors). Similar results have been reported in a series of DHB complexes.[20]

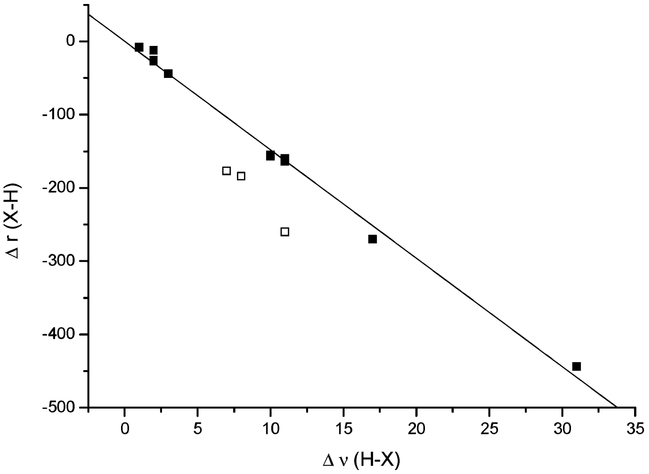

Figure 2. Variation of the H−X(C) bond length vs variation of the stretching frequency. Open squares represent the HF complexes. The linear correlation of the rest of the cases corresponds to the equation: $\Delta r(\mathrm{H-X}) = -14.80 \pm 0.02\ [\Delta\nu(\mathrm{H-X})]$, $r^2 = 0.999$.

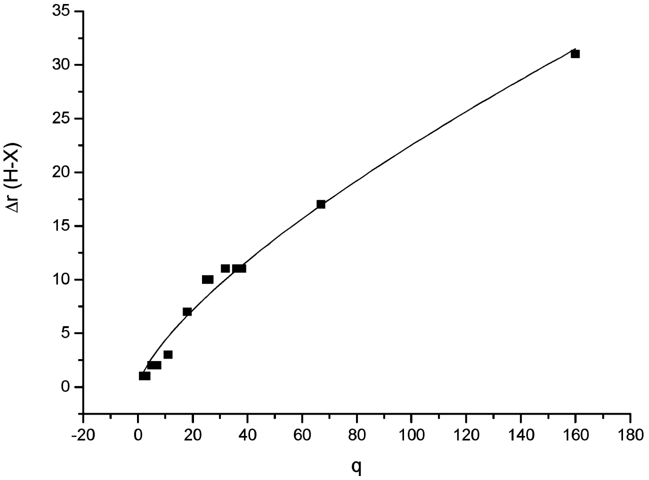

Figure 3. Variation of the H−X bond length vs orbital charge transfer. The fitted equation is $\Delta r(\mathrm{H-X}) = 0.84 \pm 0.11 \times q^{0.71\pm0.03}$, $r^2 = 0.98$.

Analysis of the dipole moment of the isolated AH_2 molecules shows that, using the same reference framework, the dipole moment direction is opposite for the BH_2 compared to the other two molecules, AlH_2 and GaH_2, whereas their values are 0.48, 0.54, and 0.32 D, respectively. While in the first case, the direction is suitable for its interaction with the dipole moment of the HX HB donors, the opposite occurs for AlH_2 and GaH_2. Thus the total dipole moment enhancement observed within the complexes is larger in the AlH_2 and GaH_2 cases than in the BH_2 case for the same HB donor, even though in the latter case the binding energy is larger.

The H−X covalent bonds are lengthened by 1−31 mÅ upon complex formation. In the same vein, red shifts in the stretching frequency associated with the HB donor molecules are observed for all complexes. The largest values correspond to the H−Br stretch of the $H_2B\cdots HBr$ complex (444 cm^{-1}). The elongation of the H−X bond and the variation of the bond stretching are linearly related, as shown in Figure 2. This relationship is in agreement with the linear relationship found between the experimental X−H stretching frequencies and the HB distance.[21]

The charge transfer from the occupied orbital of the A atom to the antibonding σ^* MO of HX, q, is expected to weaken and elongate the latter bond. An exponential relationship has been found between these two parameters for the cases studied here (Figure 3).

Dihydrogen-Bonded (DHB) Complexes. The second part of this work investigates the dihydrogen-bonded association of the same compounds (Figure 1, configuration II and III). The resulting structures contain C_{2v} symmetry for the BH_2 complexes (Figure 1, configuration II), except for the $HBH\cdots HF$ complex, which is of C_s type. The optimized complexes containing AlH_2 and GaH_2 are of C_s symmetry (Figure 1, configuration III). All attempts to obtain structures of configuration III for the BH_2 complexes spontaneously evolved to configuration II. All the structures obtained have been confirmed as minima at the UMP2/6-311++G(2d,2p) level of theory.

The most important results obtained for the DHB complexes have been gathered in Table 2. The binding energies show a similar range as in the SEHB cases, between −14.19 kJ/mol for the $HAlH\cdots HF$ complex to −1.57 kJ/mol for $HBH\cdots HCCH$. However, a different trend is observed when compared to the results of the SEHB complexes. In the DHB complexes, the strongest complexes for a given HB donor correspond to those of AlH_2, followed by GaH_2, and finally, the BH_2 complexes are much weaker than the other two HB acceptors. Regarding

TABLE 2: Binding Energies, Frequency Shift, and Geometrical Properties of the Complexes of AH_2 (A = B, Al, and Ga) Radicals with H−X (X = F, Cl, Br, CN, and CCH) in Configuration II and III at the UMP2/6-311++G(2d,2p) Level

complex	ΔE (kJ/mol)	BSSE (kJ/mol)	$\Delta E^{\mathrm{cp}\,a}$ (kJ/mol)	$\Delta\nu_{\mathrm{H-X(C)}}$ (cm^{-1})	$R_{\mathrm{H\cdots H(A)}}$ (Å)	$\Delta r_{\mathrm{H-X(c)}}$ (mÅ)	$\theta_{\mathrm{AH\cdots H}}$ (deg)
			Configuration II				
$BH_2\cdots HF$	−6.2	1.8	−4.4	−71	2.556	3	101
$BH_2\cdots HCl$	−4.7	1.7	−2.9	−39	2.716	3	90
$BH_2\cdots HBr$	−3.7	1.0	−2.7	−31	2.814	2	91
$BH_2\cdots HCN$	−2.9	0.9	−2.1	−12	2.965	3	93
$BH_2\cdots HCCH$	−2.5	0.9	−1.6	−5	3.088	4	88
			Configuration III				
$AlH_2\cdots HF$	−16.6	2.4	−14.2	−218	1.653	1	141
$AlH_2\cdots HCl$	−11.2	2.2	−9.0	−143	1.812	9	151
$AlH_2\cdots HBr$	−9.5	1.8	−7.8	−124	1.845	2	163
$AlH_2\cdots HCN$	−9.2	1.4	−7.8	−53	2.054	1	173
$AlH_2\cdots HCCH$	−5.4	1.2	−4.2	−14	2.231	1	173
$GaH_2\cdots HF$	−15.0	2.7	−12.3	−206	1.686	1	136
$GaH_2\cdots HCl$	−10.4	2.5	−8.0	−136	1.831	9	150
$GaH_2\cdots HBr$	−9.0	2.0	−7.0	−129	1.849	1	150
$GaH_2\cdots HCN$	−8.4	1.7	−6.7	−38	2.099	3	173
$GaH_2\cdots HCCH$	−5.1	1.5	−3.7	−13	2.252	2	169

[a] ΔE^{cp} refers to binding energy after BSSE correction.

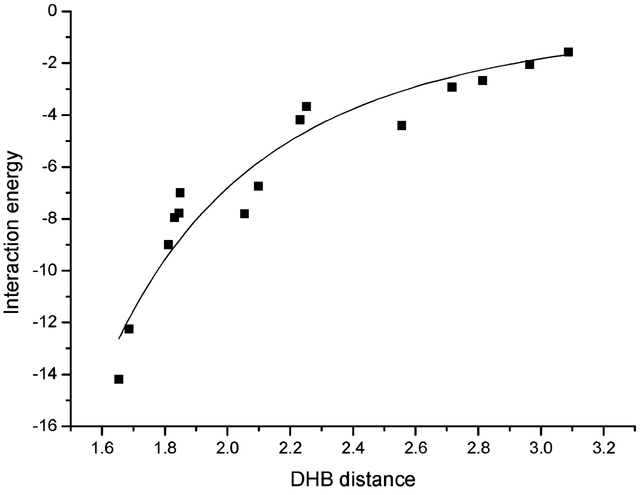

Figure 4. Binding energy (kJ/mol) vs DHB distance (Å) for the DHB complexes. The fitted curve is $E_I = -64 \pm 13 \times (\text{DHB distance})^{-3.2\pm0.3}$, $r^2 = 0.92$.

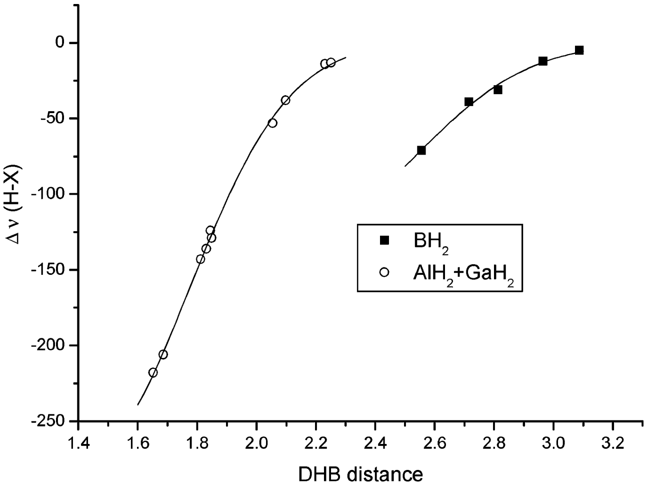

Figure 5. Red shift of the HX stretching (cm^{-1}) vs the DHB distance (Å) of the DHB systems. The exponential relationships show square correlation coefficients of 0.99 and 0.999 for the BH_2 and AlH_2+GaH_2 complexes, respectively.

the HB donor, the same ordering as before is obtained: HAH···HF > HAH···HCl > HAH···HBr > HAH···HCN > HAH···HCCH.

The interatomic distance between the two hydrogen atoms varies between 1.65 and 3.09 Å, which corresponds to the strongest and weakest complexes, respectively. The comparison of the interatomic distance vs the binding energy shows an exponential relationship between these two parameters (Figure 4). However, when larger interatomic distances have been explored, the complete curve shows a Morse-like shape.[22]

TABLE 3: Value of the Molecular Electrostatic Potential (MEP) Minima (au) and Distance (Å) to the A or H Atoms

AH_2 system	minimum close to A		minimum close to H	
	MEP	distance	MEP	distance
BH_2	−0.0252	1.919	−0.0028	1.795
AlH_2	−0.0071	2.578	−0.0206	1.372
GaH_2	−0.0081	2.599	−0.0157	1.457

The H−X bonds are stretched by the formation of the DHB complexes. The vibrational data indicate that the stretching frequencies associated with these bonds are shifted to the red, as reported in Table 2. The largest shift is obtained for the HAlH···HF complex (218 cm^{-1}), which corresponds to the most stable DHB complex. The red shift of the HB donors correlates exponentially with the DHB distance as illustrated in Figure 5. This effect is associated with a lengthening of the H−X covalent bond between 1 and 9 mÅ upon complex formation

To understand the HB behavior of the AH_2 systems, their molecular electrostatic potentials (MEPs) have been explored. In each of the three molecules, three minima have been found, one close to the A atom and two degenerate ones that correspond to the hydrogen atoms. The values of the corresponding minima and the distance to the closest atom have been collected in Table 3. In addition, the ±0.005 isocontour surfaces are depicted in Figure 6.

The MEP values explain qualitatively the binding energies of the different complexes. Thus, the MEP minimum values for each of the AH_2 molecules indicate where the stronger complex will be obtained, SEHB for the BH_2 and DHB for AlH_2 and GaH_2. A more detailed analysis shows that the MEP values of AlH_2 and GaH_2 close to the A atom are reversed with respect to the binding energies obtained for the SEHB complexes of these two molecules. In the case of the DHB structure, linear correlations with correlation coefficients larger than 0.98 are found between the binding energy and the MEP minimum values, considering each HB donor molecule separately (five families with three complexes for each one).

The position of the MEP values is, in addition, able to explain the different configuration of the DHB complexes of BH_2. In this case, the two degenerate minima found close to the

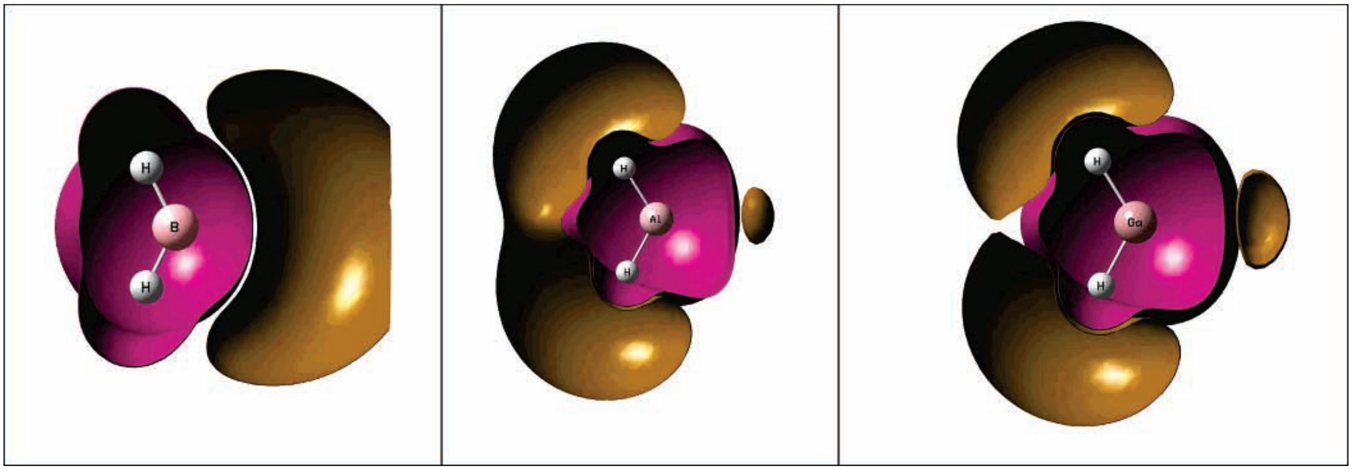

Figure 6. Molecular electrostatic potential using the 0.005 au isocontour (pink is positive and green negative) surrounding the AH_2 radicals.

hydrogen atoms are very close to the symmetry axis of the molecule, with a distance between them of 0.94 Å, while those in AlH_2 and GaH_2 are much further apart (3.35 and 3.61 Å, respectively). Thus, most of the DHB complexes of BH_2 show C_{2v} symmetry.

4. Conclusion

Two different hydrogen-bonded complexes have been found for the neutral AH_2 radical molecules (A = B, Al, and Ga). In both cases, the AH_2 molecule acts as HB acceptor, and consequently, all the atoms of these neutral systems are HB acceptors and none a HB donor. These results are unexpected for such small molecules. The relative stabilities of the different complexes have been explained on the basis of the MEP of the isolated AH_2 radical molecules. It is our hope that the present study may motivate experimentalists to search for the studied complexes of the title radicals, perhaps by matrix isolation techniques.

Supporting Information Available: Coordinates of the complexes and vibrational frequencies at the UMP2/6-311++G(2d,2p) computational level. This material is available free of charge via the Internet at http://pubs.acs.org.

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