

NMR Analysis and Hybrid-DFT Study of Three-Dimensional Aromaticity in Diborane, Dialane, Digalane and Diindane

Gh.A. Kasaei

Chemistry Department, Doroud Branch, Islamic Azad University, Doroud, Iran

D. Nori-Shargh*

Chemistry Department, Arak Branch, Islamic Azad University, Arak, Iran

H. Attar

Chemical Engineering Department, Science and Research Branch, Islamic Azad University, Tehran, Iran

H. Yahyaei

Chemistry Department, Zanjan Branch, Islamic Azad University, Zanjan, Iran

S.N. Mousavi

Chemistry Department, Arak Branch, Islamic Azad University, Arak, Iran

Abstract

Introduction: NMR analysis and hybrid-DFT based method (B3LYP/Def2-TZVPP) were used to investigate the correlation between 3-dimensional aromaticity and the dissociation energy of diborane, dialane, digalane and diindane to their corresponding monomers.

Aim: The correlation between the aromatic character and the dissociation energy of diborane, dialane, digalane and diindane to their corresponding monomers have been investigated.

Results: The results obtained showed that the dissociation energy decreases from diborane to diindane. The aromatic character of the above compounds is demonstrated by their Nucleus-Independent Chemical Shifts [NICS(0), NICS(0.2), NICS(0.4) and NICS(0.6)].

Conclusion: Interestingly, there is a significant relationship between the decrease of the in-plane σ_{22} (i.e. σ_{yy} , the plane containing H atoms bridged) chemical shift components of the NICS values and the dissociation energies of dimmers to their corresponding monomers.

Keywords: hybrid-DFT calculations, NICS, diborane, dialane, digalane, diindane

Introduction

One of the most exciting discoveries in atomic clusters in the past three decades is the existence of very stable clusters with a specific size.^[1,2] These clusters, commonly referred to as magic clusters, are characterized by low electron affinity and high ionization potential (i.e., large HOMO-LUMO gap), and enhanced stability. The magic clusters unwillingness to either accept or donate an electron makes them relatively inert and is expected to interact weakly *via* a van der Waals-like mechanism.^[3-6]

The largest range of hydride complexes is found in the third main group of the periodic table. In contrast to some 100 known binary boranes,^[7] only a handful of hydrides are

*Corresponding author

well established for aluminum and gallium. The binary hydrides of indium and thallium (InH_3 and TlH_3) are currently unknown as isolated substances. Theoretical investigations found them to be thermodynamically unstable both in the gaseous and solid state, although the prediction of a level of kinetic stability suggests that there may yet be some success in this endeavor.^[8]

There are many known volatile binary boron hydride compounds but binary aluminum hydride chemistry is limited to the polymeric $(\text{AlH}_3)_n$ solid. The spectrum of AlH_3 had already been recorded from an argon matrix, in which the target species was obtained by the co-condensation of aluminum atoms and hydrogen atoms resulting from a gas discharge.^[9] Based on the work of Andrews and Wang who obtained dibridged Al_2H_6 (a molecule that is isostructural with diborane), the reaction of laser-ablated aluminum atoms and pure H_2 during codeposition at 3.5 kelvin, following by ultraviolet irradiation and annealing to 6.5 K, allows dimerization of the intermediate AlH_3 photolysis product to form Al_2H_6 .^[10] They identified the Al_2H_6 molecule by seven infrared absorptions that were accurately predicted by quantum chemical calculations for dibridged Al_2H_6 .

$(\text{GaH}_3)_n$ prepared for the first time from GaCl_3 and LiGaH_4 ^[11] or from $\text{Ga}_2\text{H}_2(\text{CH}_3)_4$ and NEt_3 .^[12] In 1991, Downs and co-workers obtained digallane (Ga_2H_6) by successive hydrogenation starting from GaCl_3 . The first step of this synthesis is a dehalosilylation reaction of GaCl_3 with Me_3SiH (first discovered by Schmidbaur et al., which yields Cl_2GaH).^[13] The addition of two equivalents of Me_3SiH yields the very sensitive ClGaH_2 ,^[14] which then can be treated with lithium tetrahydrogallate to yield gallane in a solvent-free reaction that employs an all-glass apparatus at pressures below 10^{-4} Torr; gallane is stable only up to 240 K.^[15] Structural determination by gasphase electron diffraction was possible with difficulty due to the reaction of gallane with the photographic emulsion at pressures of about 10^{-6} mbar. Because of thermal instability and the resulting difficulties with crystal growth from the liquid phase, a determination of the solid-state structure of GaH_3 has not yet been possible. However, from investigations on polymeric gallaborane $(\text{GaBH}_6)_n$,^[16] one could be tempted to predict GaH_3 to be also polymeric in the solid state.

The elusive indium hydride InH_3 could be stabilized by donor ligands in many complexes, such as $\text{Me}_3\text{N}\cdot\text{InH}_3$ and the chinuclidine complex of InH_3 as monomeric compounds, the polymeric dabco complex $[-\text{N}(\text{C}_2\text{H}_4)_3\text{N}\cdot\text{InH}_3-]_n$, the mono- and diphosphane complexes $\text{R}_3\text{P}\cdot\text{InH}_3$ and $(\text{R}_3\text{P})_2\cdot\text{InH}_3$, and even InH_3 adducts of Arduengo carbenes.^[17] It should be noted that some of these compounds are only stable at low temperatures. The direct application of indium hydrides in organic synthesis has been reported for the chemoselective reduction of functionalized benzaldehydes, conjugated alkenes and unsaturated nitriles, as well as for hydroindation. The reagents for such reactions are dichloroindane (HInCl_2) which is obtained from the reaction of InCl_3 with Bu_3SnH or NaBH_4 , and is found to be stable as a solution in THF at room temperature.^[18]

Our present study was originated to give an answer to the following question: is there correlation between the aromatic character of diborane, dialane, digalane and diindane and the dissociation energies to their corresponding monomers?

A literature review revealed that the correlations between the aromatic character of diborane, dialane, digalane and diindane and the dissociation energies to their corresponding monomers have not yet been reported. In this work, the quantitative relationship between the aromatic character^[19,20] of above compounds and the dissociation energies to their corresponding monomers is demonstrated by nucleus-independent-chemical-shift (NICS) values.^[21]

Computational details

Hybrid-DFT (B3LYP)^[22,23] calculations (with Def2-TZVPP²⁴ basis sets) were performed using the GAUSSIAN 03 package of programs.^[25] Energy minimum molecular

geometries were located by minimizing energy, with respect to all geometrical coordinates without imposing any symmetry constraints. The nature of the stationary points for compounds **1-4** has been determined by means of the number of imaginary frequencies. For the minimum state structure, only real frequency values were accepted, and in the transition-state structure, only single imaginary frequency value was accepted.^[26,27]

Also, we used the GIAO-B3LYP/Def2-TZVPP method in order to calculate the nucleus-independent chemical shift (NICS) values. The experimental values of the NMR chemical shifts are vibrational average, whereas the computational results correspond to a fixed geometry at 0 K. It should be remembered that the NMR chemical shifts are not too sensitive to the optimized geometry.^[28]

Results and Discussion

The values of the thermodynamic functions H , S , G and the ΔG , ΔS and ΔH parameters for diborane, dialane, digalane and diindane and the dissociation energies to their corresponding monomers as calculated at the B3LYP/Def2-TZVPP level of theory, are given in Table 1. As it can be seen, ΔS values are relatively small, so that the calculated ΔH and ΔG parameters are close to the ΔE_0 values.

Table 1- B3LYP/Def2-TZVPP calculated thermodynamic parameters [ΔH , ΔG (in hartree) and ΔS (in cal mol⁻¹K⁻¹)], for diborane (B₂H₆), dialane (Al₂H₆), digalane (Ga₂H₆), diindane (In₂H₆) and their corresponding monomers.

Geometries	H(Hartree)	S(cal mol ⁻¹ K ⁻¹)	G(Hartree)	ΔH^a (Hartree)	ΔS^a (calmol ⁻¹ K ⁻¹)	ΔG^a (Hartree)
B₂H₆	-53.245062	58.146	-53.272689	0.000000 (0.000000) ^b	0.000000	0.000000 (0.000000) ^b
2 BH₃	-53.190824	70.608	-53.224372	(0.054238) (34.0) ^b	12.462	(0.048317) (30.3) ^b
Al₂H₆	-488.469775	68.326	-488.502239	0.000000 (0.000000) ^b	0.000000	0.000000 (0.000000) ^b
2 AlH₃	-488.421894	82.816	-488.461243	(0.047881) (30.0) ^b	14.49	(0.040996) (25.7) ^b
Ga₂H₆	-853.346297	73.709	-853.381319	0.000000 (0.000000) ^b	0.000000	0.000000 (0.000000) ^b
2 GaH₃	-853.313677	82.137	-853.352703	0.03262 (20.5) ^b	8.428	0.028616 (17.9) ^b
In₂H₆	-383.919756	79.754	-383.957649	0.000000 (0.000000) ^b	0.000000	0.000000 (0.000000) ^b
2 InH₃	-383.892936	84.757	-383.933207	0.02682 (16.8298182) ^b	5.003	0.024442 (15.3) ^b

^a Relative to the ground state. ^b Numbers in parenthesis are in kcal mol⁻¹

Based on the B3LYP/Def2-TZVPP results, the calculated Gibbs free energy values between diborane, dialane, digalane and diindane and their corresponding monomers (i.e. $\Delta G_{2\text{monomer-dimer}}$) decrease from diborane to diindane (see Table 1 and Fig. 1). The calculated $\Delta G_{2\text{monomer-dimer}}$ for the dissociation processes of diborane, dialane, digalane and diindane to

their corresponding monomers are 30.3, 25.7, 17.9 and 15.3 kcal mol⁻¹, respectively, as calculated at the B3LYP/Def2-TZVPP level of theory.

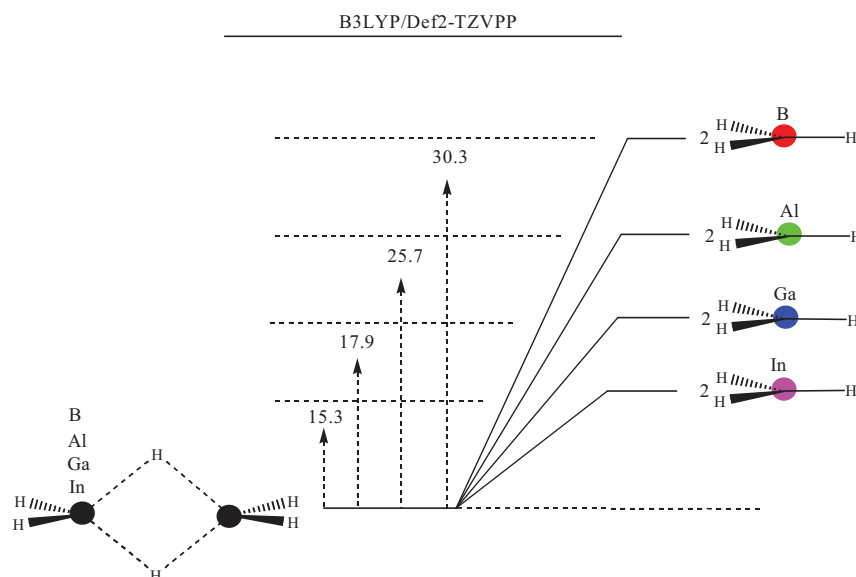
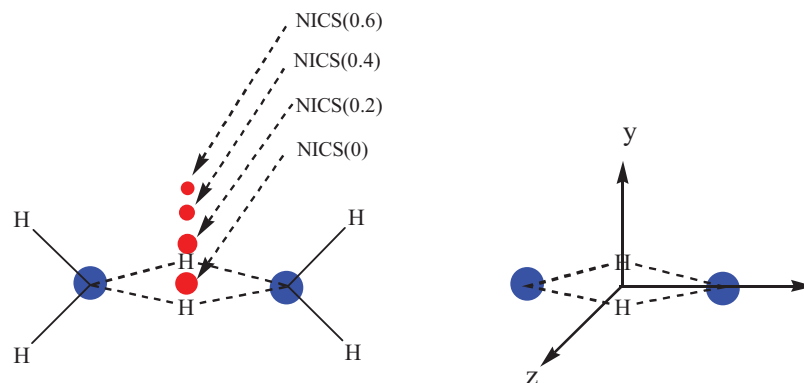


Figure 1- B3LYP/Def2-TZVPP calculated free energy profiles of the dissociation energy of diborane, dialane, digalane and diindane to their corresponding monomers.

The nucleus-independent-chemical-shift (NICS) values for the four-membered rings of diborane, dialane, digalane and diindane arise from same mechanism. The NICS values calculated can be used to compare the aromaticity for the same types of molecules.



Scheme

GIAO-B3LYP/Def2-TZVPP calculated NICS values at the approximate centers of the four-membered rings of diborane, dialane, digalane and diindane, NICS(0), are -26.4, -9.3, -15.2 and -12.9 ppm, respectively (the NICS values are reported as the negative of the actual size) (see Scheme 2). The NICS(0) values are dominated by the in-plane σ_{33} chemical shift components (see Table 2). The in-plane σ_{33} chemical shift (with their actual size) components at the approximate centers of the four-membered rings of diborane, dialane, digalane and diindane are 38.7, 12.6, 42.6 and 49.0 ppm, respectively.

The NICS(0.2), NICS(0.4), NICS(0.6), NICS(0.8), NICS(1.0), NICS(1.2) and NICS(1.4) values are obtained above the plane on a line passing through the point where NICS(0) values were evaluated (see Table 2). The GIAO-B3LYP/Def2-TZVPP in-plane σ_{22}

(i.e. σ_{yy} , see scheme 2) chemical shift components (with their actual size) at the approximate centers of the four-membered rings of diborane, dialane, digalane and diindane are 21.7, 12.0, 7.1 and 0.8 ppm, respectively. Based on the results obtained, the calculated values of the in-plane σ_{22} chemical shift components at the approximate centers of the four-membered rings decrease from four-membered rings of diborane to diindane. This trend observes for the values of the in-plane σ_{22} chemical shift components of NICS(0.2), NICS(0.4) and NICS(0.6) (see Table 2). The decrease of the in-plane σ_{22} chemical shift components of NICS(0.2), NICS(0.4) and NICS(0.6) is in excellent agreement with the decrease of the calculated $\Delta G_{2\text{monomer-dimer}}$ values for the dissociation processes from diborane to diindane (see Tables 1, 2).

Table 2- GIAO-B3LYP/Def2-TZVPP calculations of the absolute chemical shifts, σ_{iso} , and chemical shift tensor components (ppm) for B_2H_6 , Al_2H_6 , Ga_2H_6 and In_2H_6 .

Compound	B_2H_6	Al_2H_6	Ga_2H_6	In_2H_6
NICS(0.0)				
σ_{iso}	-26.3639	-9.3239	-15.2471	-12.8986
σ_{11}	18.7152	3.3269	-3.9636	-11.1419
σ_{22}	21.6635	12.0365	7.1081	0.8334
σ_{33}	38.7129	12.6082	42.5969	49.0041
NICS(0.2)				
σ_{iso}	-23.6840	-8.8714	-14.4029	-12.2689
σ_{11}	17.5767	3.6086	-2.7908	-9.8742
σ_{22}	19.9606	11.4319	5.8351	-0.0636
σ_{33}	33.5146	11.5736	40.1645	46.7446
NICS(0.4)				
σ_{iso}	-17.4508	-7.6891	-12.1832	-10.6079
σ_{11}	14.9381	4.2238	0.0572	-6.5074
σ_{22}	15.9304	8.9195	2.5872	-2.4093
σ_{33}	21.4839	9.9241	33.9052	40.7404
NICS(0.6)				
σ_{iso}	-10.9650	-6.1454	-9.3203	-8.3999
σ_{11}	9.3921	4.7895	-1.3534	-5.2796
σ_{22}	11.4249	5.5323	3.2162	-2.3202
σ_{33}	12.0778	8.1144	26.0981	32.7996
NICS(0.8)				
σ_{iso}	-6.1048	-4.6076	-6.5711	-6.1853
σ_{11}	0.8963	2.3999	-4.7318	-7.7970
σ_{22}	7.8299	4.9123	5.6451	1.5629
σ_{33}	9.5883	6.5105	18.8000	24.7900
NICS(1.0)				
σ_{iso}	-3.1158	-3.3013	-4.3707	-4.3213
σ_{11}	-3.6230	-0.0255	-6.8898	-9.3857
σ_{22}	5.5049	4.6586	6.9746	4.4419
σ_{33}	7.4654	5.2709	13.0271	17.9079
NICS(1.2)				

Table2 – continued ...

σ_{iso}	-1.4644	-2.3298	-2.8355	-2.9330
σ_{11}	-5.4134	-1.5763	-7.7966	-9.9913
σ_{22}	4.2064	4.2094	7.4113	6.2196
σ_{33}	5.6003	4.3562	8.8919	12.5708

	NICS(1.4)			
σ_{iso}	-0.6237	-1.6566	-1.8510	-1.9845
σ_{11}	-5.6181	-2.4107	-7.7687	-9.7953
σ_{22}	3.5519	3.6225	6.0543	7.0680
σ_{33}	3.9372	3.7581	7.2674	8.6809

Representative structural parameters for diborane, dialane, digalane, diindane and their corresponding monomers (i.e. borane, alane, galane, indane), as calculated at the B3LYP/Def2-TZVPP level of theory, are shown in Fig. 2). Although it is not expected, in principal, to obtain exactly the experimental values because of the differences in definition of bond length values, it is possible to carry out theoretical calculations, from which many properties and structures can be obtained with an accuracy that is competitive with experiments.

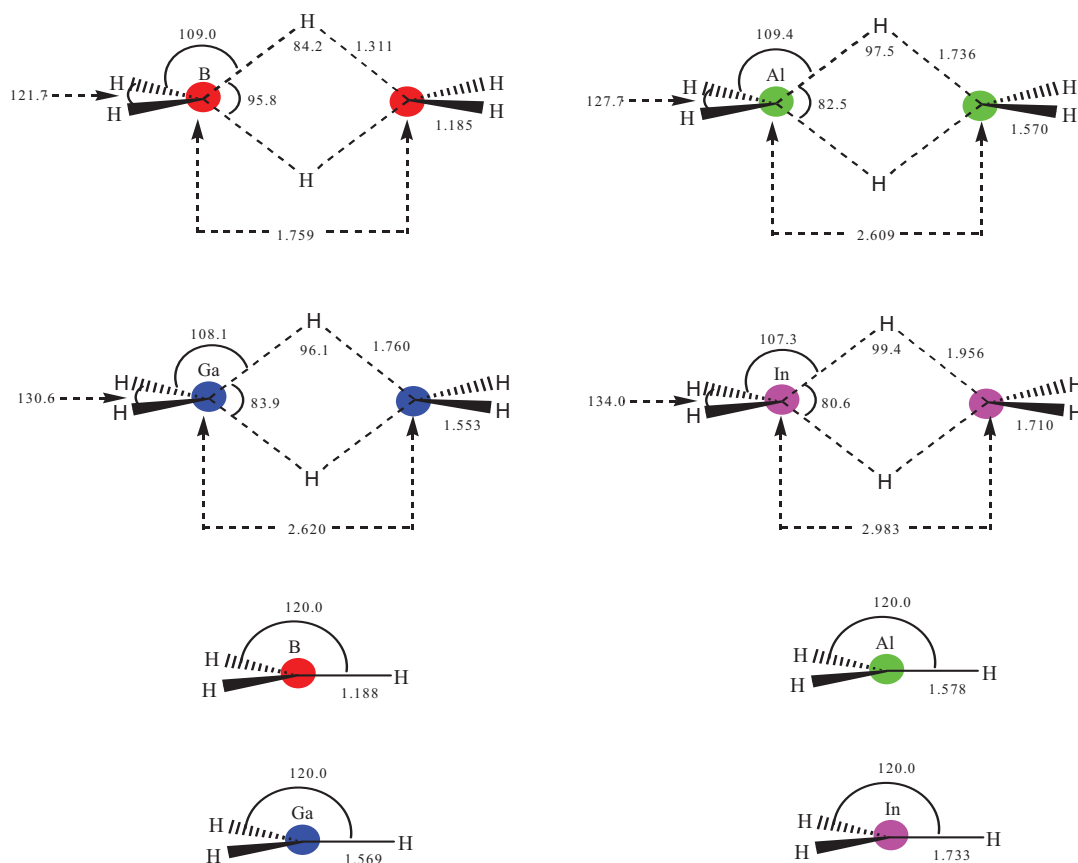


Fig 2- B3LYP/Def2-TZVPP calculated structural parameters of diborane, dialane, digalane and diindane. The calculated bond length and bond angle values are in angstrom (Å) and degree (°), respectively.

The heavy atom distances increase from diborane to diindane. The B3LYP/Def2-TZVPP results show that the heavy atom distances in diborane, dialane, digalane and diindane are 1.579, 2.609, 2.620 and 2.983 Å, respectively. Also, the bridged heavy atom-H bond lengths increase from diborane to diindane but there is no smooth variation for the terminal heavy atom-H bond lengths. The calculated bridged heavy atom-H bond lengths in diborane, dialane, digalane and diindane are 1.311, 1.736, 1.760 and 1.956 Å, respectively, while for bridged heavy atom-H bonds are 1.185, 1.570, 1.553 and 1.710 Å. The variations of the in-plane σ_{22} chemical shift components of NICS(0.2), NICS(0.4) and NICS(0.6) and the calculated $\Delta G_{2\text{monomer-dimer}}$ values for the dissociation processes are in accordance with the variation of the calculated bridged heavy atom-H bond lengths in diborane, dialane, digalane and diindane (see Tables 1, 2).

Conclusions

The B3LYP/Def2-TZVPP calculations reported above and NMR analysis provided a reasonable picture from energetic, structural and bonding points of view for diborane, dialane, digalane and diindane. Effectively, the B3LYP/Def2-TZVPP results showed that the calculated $\Delta G_{2\text{monomer-dimer}}$ values for the dissociation processes decrease from diborane to diindane. This fact can be explained by the crease of the in-plane σ_{22} chemical shift components of NICS(0.2), NICS(0.4) and NICS(0.6) from diborane to diindane. In addition, the calculated $\Delta G_{2\text{monomer-dimer}}$ values for the dissociation processes are in accordance with the variation of the calculated bridged heavy atom-H bond lengths.

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