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Are closed clusters expected from the $(n + 1)$ skeletal electron pairs rule in alanes and gallanes? A DFT structural study of A_nH_{n+2} (A = Al, Ga, and n = 4–6)

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ABSTRACT

It has been suggested recently that the alanes Al_nH_{n+2} can be treated by the polyhedral skeletal electron pair theory (PSEPT) of Wade and Mingos (W–M) as it was successful for their borane congeners such as B_nH_{n+2}, well known as the deprotonated $B_nH_n^{2-}$. To do so, the neutral Al_nH_{n+2} have been considered as $Al_nH_n^{2-} + 2H^+$. The additional hydrogens donate their electrons to the Al_nH_n polyhedral framework and according to the $n + 1$ electron pairs rule; these clusters should have *closo*-polyhedral structures. In this work the homologous gallanes, the structures and stabilities of Ga_nH_{n+2} are studied at high levels of calculational theory and we investigated the applicability of the W–M rule to the alanes and gallanes A_nH_{n+2} (n = 4–6; A = Al, Ga). It will be shown that the presence of bridging hydrogen atoms reduces the compactness of the corresponding polyhedron and so these species do not have the closed structures. The computations were performed at B3LYP/6-311+G(d,p), BPW91/6-311G(d,p) and B3LYP/6-311+G(3df,2p) levels of theory. Our interest in these compounds includes their potential use as hydrogen storage species and future clean sources of energy.

1. Introduction

After carbon, the elements of 13th group have become the second candidates to form hydride compounds A_nH_m (A = B, Al, Ga, ...). Boron is the first element having a large number of this class of compounds. Aluminum occupies the second range and now is receiving considerable interest in this last decade both experimentally as well as theoretically [1–10]. Although the first alane AlH_3 and gallane GaH_3 were known since the forties of the last century [11] in dimeric form, the literature is still sparse with regards to hydrido-aluminum and gallium data.

This end of the first decade of the XXIst century has shown considerable progress in the chemistry of hydrides of 13th group elements especially in the alanes field. In fact, much as numerous boranes have $B_nH_n^{2-}$ as a general formula for species whose structural properties have been extensively studied, alanes Al_nH_m (n = 4, 5, ..., $m = n + 2$, $n + 4$) have been the subject of multiple studies [5–10] since 2007 after the reported mass spectroscopic analysis by Bowen and his group [5,6] showing the corresponding evident stability of Al_4H_6, Al_5H_7, Al_6H_8 and related species. Nevertheless, the geometrical structures has remained the subject of controversy since only the empirical formula Al_nH_m was experimentally accessible by means of mass spectroscopy equipped with a pulsed arc cluster ions discharge source (PACIS). The published structures result from computations at different levels of theory [5–10]. The accuracy depends on the level of basis set used for the description of the molecular wave functions. Moreover, it has been argued that such systems geometries obey the polyhedral skeletal electron pair theory (PSEPT) of Wade and Mingos (W–M) [12–15] which was based on the electron counting, especially powerful was the $(n + 1)$ electrons pairs rule whose application has been successful for $B_nH_n^{2-}$ borane ions. The related Al_nH_{n+2} clusters have been considered as protonated $Al_nH_n^{2-}$ where two hydrogen atoms donate their electrons to the heavy atom polyhedron. Hence, as it is expected by the W–M rule, the structure should be a closed polyhedron where the n heavy atoms occupy n vertices and there are two bridged edges. This systematic application of such rule deserves a deep analysis because the lowest structure in energy is not always a closed polyhedron, and indeed there is sometimes a slight but significant energy difference between a closed and a totally opened configuration on the potential energy surface (PES).

In this work we present an investigation of gallanes Ga_nH_{n+2} (n = 4, 5, and 6) species homologous to the alanes. These compounds have not yet been reported experimentally. We also try to draw a comparison of these two families of compounds with the corresponding double anionic boranes $B_nH_n^{2-}$, species taken as reference for W–M rules proceeding along the 13th column of the periodic table. This analysis will permit us to make conclusions about the general applicability of such W–M rules for these hydrides.

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2. Computational detail

In the beginning, all possible structures have been considered after imposing some geometrical restrictions in order to maintain the molecular symmetry. After that, the symmetry group is stepwise lowered by relaxing some geometrical parameters until finally treating them in C_1 symmetry on the total PES with 24, 30, and 36 degrees of freedom ($3n - 6$, $n = 10$, 12, 14, total number of atoms) for A_4H_6, A_5H_7, A_6H_8, respectively. Calculations were performed using density functional theory (DFT) by means of the B3LYP [16–18] and B3PW91 [19–23] functionals and 6-311+G(d,p) and 6-311+G(3df,2p) basis sets for the first and 6-311G(d,p) for the second functional, respectively. Each structure has been characterized by a vibrational calculation by diagonalizing the second derivative matrix of the energy. All the presented structures are minima (all frequencies are positive) as opposed to transition states with one imaginary frequency. We have also evaluated the HOMO–LUMO energy gaps of the corresponding anions of absolute minima using the TD–DFT method [24–28]. To perform these calculations, the GAUSSIAN03 series of programs [29] was used.

3. Results and discussion

The main findings from the works of Bowen and his coworkers, are (i) the stoichiometries of the atoms constituting the alanes molecular systems (i.e. chemical formulas) from their mass-spectroscopy–PACIS technique and (ii) the stabilities of these compounds by the determination of HOMO–LUMO energy gaps from the PES according to Koopmans' approximation [30]. However, (iii) the geometrical structure was also obtained by these authors' theoretical calculations at (B3PW91/6-311G(d,p)) level. It has been concluded [5,6] that Al_nH_{n+2} could be structurally understood as $Al_nH_n^{2-}$ and treated by the $n + 1$ electron pairs rule of the PSEPT model, well-known as the W–M model [11–14], so successfully applied in the boranes compounds. It could be summarized for 13th group elements clusters like $A_nH_n^{2-}$ (A = B, Al, Ga, ...) having n heavy atoms (each one has three valence electrons) located on n vertices, the structural geometry of heavy atoms would be (i) *closo* when there are $n + 1$ bonding electron pairs, (ii) *nido* when there are $n + 2$ bonding electron pairs are available and (iii) *arachno* when $n + 3$ electron pairs constitute the heavy atoms cage binding. For example the cluster $B_4H_4^{2-}$ uses nine pairs of electrons (*12* electrons from borons plus *4* from hydrogens and *2* from the 2− charges). The B–H bonds use *4* pairs and the remaining *5* pairs ($n + 1$, $n = 4$) are used to hold the borons together in a tetrahedron (*closo*) arrangement. We have evaluated the compactness by comparing the average distance d_{A-A} (A = heavy atom) between the heavy atoms calculated as:

$$d_{A-A} = \frac{\sum_i^{n-1}\sum_{j>i}^{n}(d_{A_i-A_j})}{C_n^2}$$

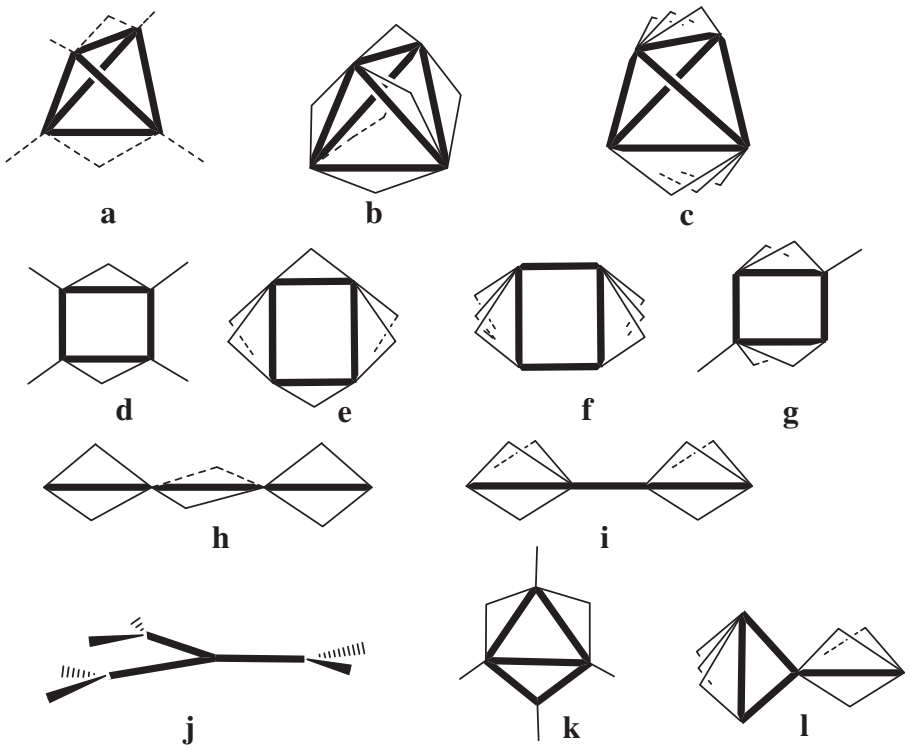
C_n^2: number of combinations of *2* among n heavy atoms.

This average distance d_{A-A} increases with the opening of the cluster so the cage compactness decreases on going from a closed cluster to increasingly more open clusters.

We have recomputed the tetra, penta and hexa-alanes (see structures **1–9**, **15–18**, and **23–26** in Supplementary material) and the corresponding gallanes at three levels of theory (see Computational detail section). Like previous works of Martínez [7] and Ding [8,10] and their coworkers, our results are consistent for the alanes with Bowen's findings only for the Al_4H_6 case, nevertheless we have noted considerable divergence when we increase the level of computation in the other cases.

3.1. Tetragallane(*6*)

A meticulous PES exploration has been undertaken by a preliminary optimization using the higher symmetry of each geometrical configuration of models depicted in Scheme 1 (ideal structures **a–l**). After that, we proceeded on a stepwise relaxing of structural



Scheme 1. Ideal structures, starting points of optimization.