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The hyperconjugation effect on the graphene counterparts based on silicon and germanium

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ABSTRACT

Bending of the A = A (A of the group IVA) double bond neighboring is rationalized by the hyperconjugation phenomenon analysis. The bending is also observed for the high sized linear, cyclic or graphene-like compounds that imply the conjugated double bonds. The electronic delocalization takes place between occupied $\sigma(\pi)$ and unoccupied $\pi^*(\sigma^*)$ orbitals especially for compound implying Si and Ge atoms. Leading to rippled structure, this phenomenon affects the silicene and germane thickness sheets and probably would have some consequences on the properties of such compounds when they will be involved in the industries in the future. However we introduce a new parameter to assess the thickness of graphenic structures when the hyperconjugation takes place in the bonding framework. The study has been undertaken at high levels of theory like B3LYP/6-311 + G(3df,2p).

1. Introduction

Since the first announcement of identification and analysis of the graphene in 2004 [1], a highly heated race stands between different research groups all over the world that it is not easy to make an inventory of published works to date (more than 3500 reviewed papers are published since 2004). The literature does not stop getting riche of precious data stating that this compound is worthy of "revolutionary compound" quality.

Graphene structure is a flat monolayer of sp^2 hybridized carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice. This structure gives it significant properties. Silicon and germanium-based Graphene counterparts, called silicene and germanene respectively, have also been identified [2–12] although their preparation is still not as easy as graphene's one.

However, some structural and physical properties of these compounds are already known like their rippled honeycomb structure. This would give to the silicone, for example a high advantage, to be integrated in nanoelectronics devices given that silicon compounds are ubiquitous in electronic circuits and components.

Graphene, silicene and germanene (maybe stanene and plumbene) exhibit, all, honeycomb lattice structures but only the first one has a smooth structure while the others are rippled. In fact, hexacycles forming the layer of graphene are planar having a D_{6h} local symmetry whereas this local symmetry is D_{3d} in the others. As the physical properties depend on such structures [13–16], some research groups have been interested in the factors behind the buckled behavior of silicene, germanene and others [13,17–22]. Their analysis's was focused on the Pseudo Jahn Teller effect which is due to the ground state and the lowest excited ones coupling.

In this work, we try to highlight some effects leading to the buckled structures but from a hyperconjugation phenomenon point of view. This phenomenon take place between some bonds orbitales and some virtual ones. In fact as the double bond conjugation is the backbone of all higher-sized compounds, the analysis will be undertaken from the isolated double bound to graphenic systems via the hexacyclic metalenes. We will also show how this phenomenon affects the global thickness of the graphene-like

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compounds since this parameter should highly important in the use of such materials in the electronic factories.

2. Computation details

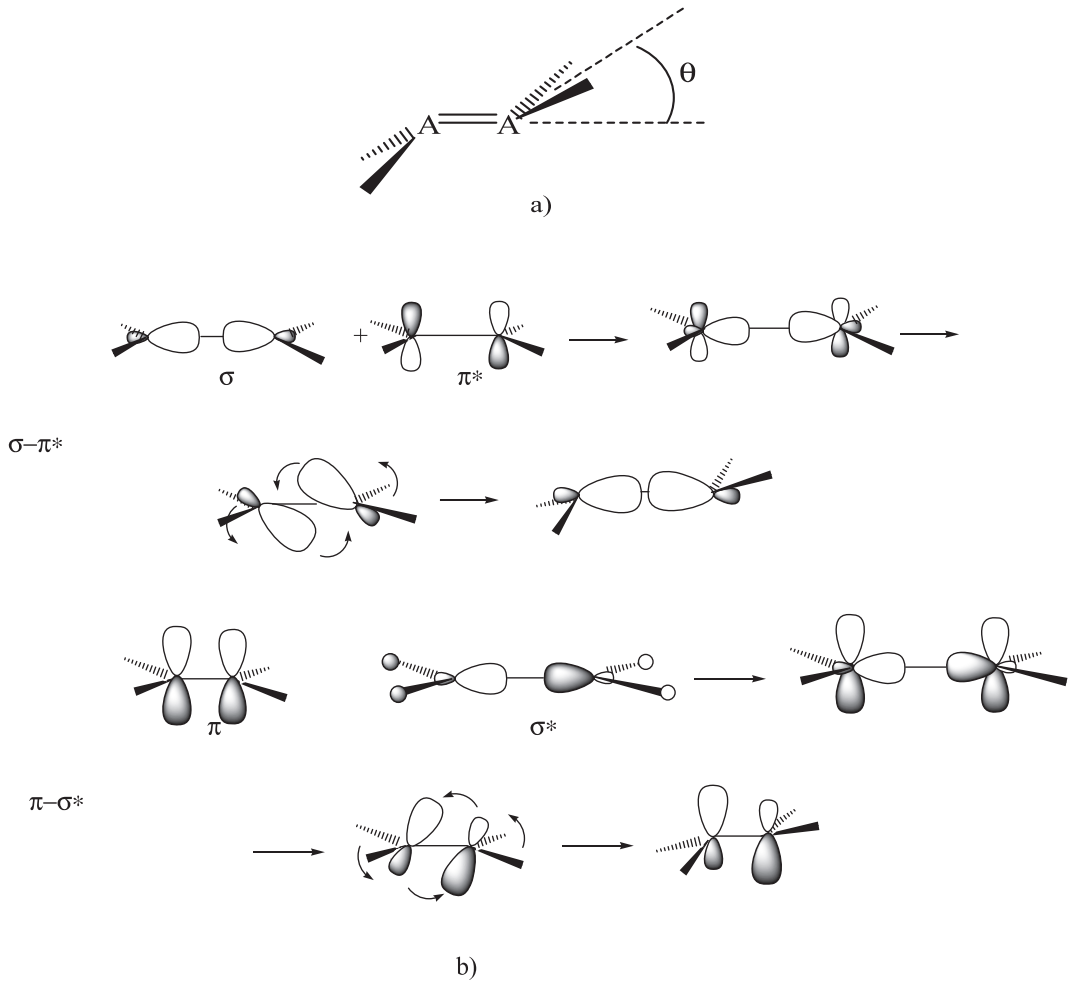
All calculations have been undertaken using the Gaussian09 series of computer programs [23]. The geometrical optimization was performed firstly for each system in its highest symmetry after that a stepwise geometrical parameters relaxation has been followed until the treatment without restrictions. The density functional theory (DFT) with B3LYP functional [24,25] has been adopted with the 6-311 + G(3df,2p) basis set [26,27]. Effects of hyperconjugative interactions were investigated using the natural bond orbitals (NBO) partitioning scheme [28]. The interacting orbitals responsible of this phenomenon were identified by the NBO treatment and the corresponding interactions were assessed by the freezing of the corresponding Fij elements of the non-diagonal elements of the Fock matrix.

3. Result and discussion

3.1. A-A (A = Si, Ge) double bond

Unlike ethylenic compounds where the double bond is well-defined as flat structure, the corresponding counterparts $R_2A = AR_2$ (A from group IVA heavier than C seem to be *trans*-bent, R is an organic or inorganic radical) (Scheme 1a) [29–33]. There are many reports in the literature where the phenomenon is explained from the spin-state point of view [31,34–40]. But recently, it has been explained as a result of an electronic delocalization between occupied σ (or π) and virtual π*(or σ*) orbitals (Scheme 1b) [31–33,41,42]. To treat computationally this problem, it's necessary to perform the calculation at high levels of theory since the observation of the phenomenon depend on the calculation quality: method, basis set of wave function development and electronic correlation [4–6,25–27,43–45].

In fact detailed energetic analysis of orbital interactions in terms of natural bond orbital (NBO) shows that a hyperconjugation phenomenon based on electron delocalization between occupied MOs and other virtual ones, increases while describing the series A_2H_4 (A: element of group IVA) from carbon to lead. This delocalization involves the interaction between the occupied σ(or π) orbital and the virtual π* (or σ*) one (Scheme 1 b). Since, as well σ as σ* are spread over the A-H bonds, such interactions affect the flatness of the heavy atoms vicinity. This deformation (folding) increases when the energetic gaps $\Delta E_{\sigma-\pi^*}$ and $\Delta E_{\pi-\sigma^*}$ decreases. To account for these interactions, we carried out some calculations by freezing F_{ij} elements of the off-diagonal Fock matrix in the energetic contribution E_{ij} [42].



Scheme 1. a) Trans bent structure of A_2R_4 (A = Si-Pb), b) Interactions behind the hyperconjugation phenomenon.