Vibrational spectra and ab initio analysis of *tert*-butyl, trimethylsilyl, trimethylgermyl, trimethylstannyl and trimethylplumbyl derivatives of 3,3-dimethylcyclopropene. XI. Secondary periodicity

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ABSTRACT

Regularities of changes in the structural parameters and vibrational wavenumbers for certain moieties of the title compounds are presented. The optimized geometrical parameters and the force fields of the di- and monosubstituted 3,3-dimethylcyclopropenes were determined at the HF/3-21G* and HF/DDAll pseudopotential levels, respectively. These theoretical levels were chosen because of peculiarities of Gaussian 03 suite of programs for the Sn and Pb atoms. The theoretical vibrational wavenumbers were calculated using the corresponding scaled force fields. The regularities obtained in the form of zigzag lines for the properties as a function of the period number of X in the Mendeleyev Periodic Table are analogous to regularities that are characteristic of properties of the atoms of the 14 (IVA) group. This is known as the secondary periodicity phenomenon.

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1. Introduction

The term "secondary periodicity" was introduced by Biron in his paper published in 1915 [1]. Using a series of reactions as examples, he considered the ability of the group 15 elements (N, P, As, Sb, and Bi) to transform from the trivalent state into the pentavalent state. To represent the changes in this ability, Biron sketched arrows like this: N ↗ P ↘ As ↗ Sb ↘ Bi. Biron named the zigzag course of changes in this ability as a function of the atomic numbers of the group 15 elements, "secondary periodicity". He noted that other physical properties of the atoms and of compounds including them are bound to follow this secondary periodicity. Indeed, the representation in Fig. 1 of the sums of the first, second, third and fourth ionization potentials of the group 14 elements (C, Si, Ge, Sn, or Pb) [2] reveals an analogous zigzag broken line.

In general, it is known that changes in some molecular properties are not monotonic down the groups of elements. This regularity for the *p*-block elements is explained by shielding of the nuclear charges for valence electrons by the completely filled 3*d* and 4*f* shells and by the peculiarities of the electron correlation effects.

It is of interest to test this regularity for the quantum-chemically calculated bond lengths and vibrational wavenumbers of the title compounds. The set of the chemical compounds under investigation is not connected with the goal of demonstration of secondary periodicity. Conversely, the secondary periodicity effects are used to explain some experimental and calculated results obtained in the course of our investigations mentioned below.

2. Calculations

The Gaussian 03 program package (G03) [3] was used to optimize the geometries, calculate the force fields and vibrational wavenumbers of the 3,3-dimethylcyclopropenes substituted by $(CH_3)_3X–$ at the 1 and 2 positions (X = C, Si, Ge and Sn; Fig. 2) or at the 1 position (X = C, Si, Ge, Sn and Pb; Fig. 3).

For the disubstituted derivatives the calculations were performed using the HF/3-21G* basis set (G03 does not include this basis set for Pb) and the vibrational wavenumbers were determined at the HF/3-21G*//HF/3-21G* level [4]. For the monosubstituted

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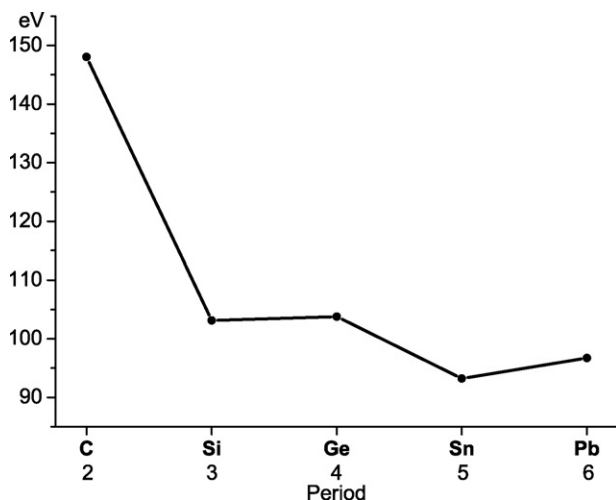
Fig. 1. Broken line constructed for the sums of the first, second, third, and fourth ionization potentials of the group 14 elements (C, Si, Ge, Sn, or Pb): 148.0254, 103.1324, 103.7715, 93.21368, 96.70825 eV.

derivatives all the calculations were carried out at the HF/SDDAll pseudopotential level [5]. Earlier, the corresponding calculations were performed for the first three molecules of each series at the HF/6-31G* level (see references in Refs. [4,5]).

The well-known procedure of scaling the quantum-chemical force fields F [6–8] was used according to the equation $\Phi = DFD$, i.e. the congruent transformation. D is the diagonal matrix of the scale factors. A set of scale factors for correction of the corresponding force fields was determined using the experimental wavenumbers of 3,3-dimethyl-1-(trimethylsilyl)cyclopropene [9].

Note that the calculations were performed without taking into account relativistic effects. However, the good agreement between the wavenumbers calculated from the scaled quantum-chemical force fields and the experimental wavenumbers reveals that either the relativistic effects are rather small for the title molecules or that the accuracy of our calculations is not sufficient to detect these effects [4,5].
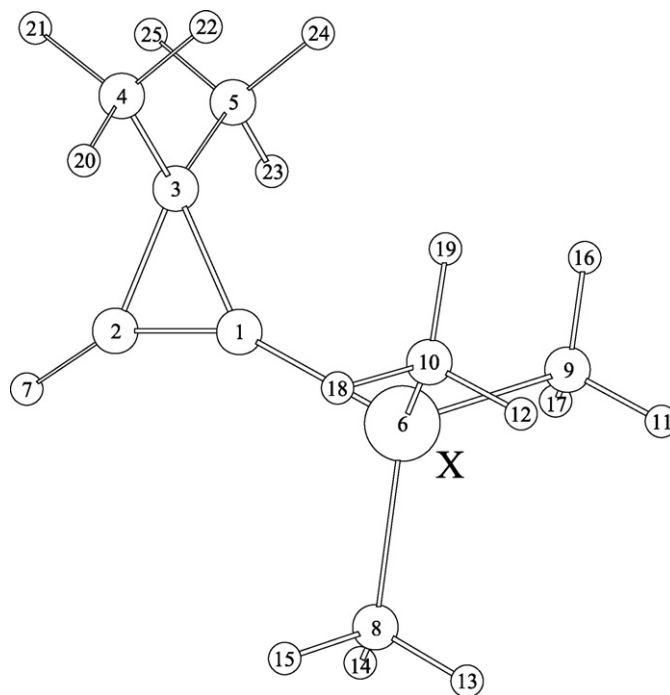

Fig. 3. Molecular model of 3,3-dimethyl-1-(X(CH$_3$)$_3$)cyclopropene where X = C, Si, Ge, Sn, or Pb.

3. Discussion

With increasing period number of the heteroatom X (Figs. 2 and 3), the properties of the moieties including or connecting to the atoms undergo various changes. For example, the formal bond lengths increase, the force constants decrease, and the vibrational wavenumbers also decrease. However the character of these changes remains approximately similar. To appreciate the significance of this statement, selected optimized interatomic distances (Fig. 4), scaled diagonal force constants (Fig. 5), and experimental or calculated wavenumbers of the structural fragments (Fig. 6) of the disubstituted 3,3-dimethylcyclopropenes
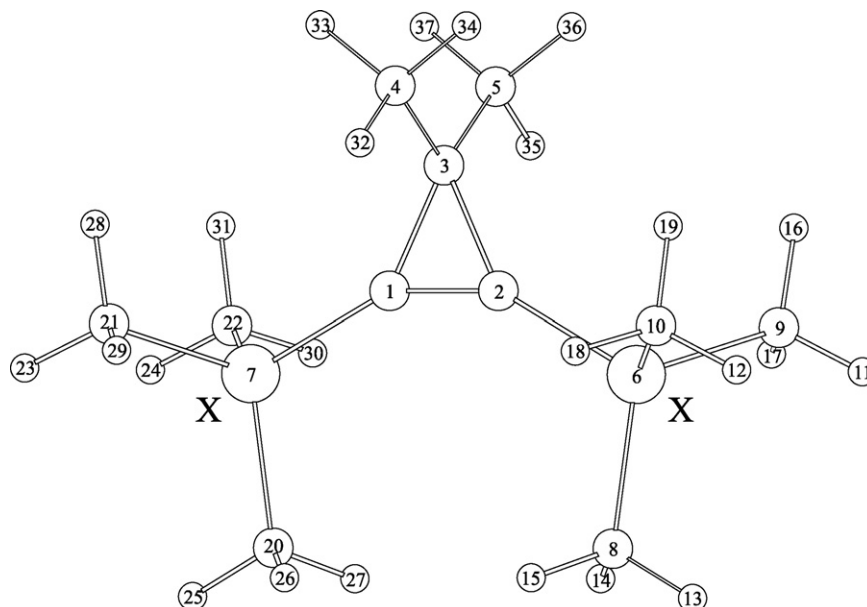

Fig. 2. Molecular model of 3,3-dimethyl-1,2-bis(X(CH$_3$)$_3$)cyclopropene where X = C, Si, Ge, or Sn.