Analyzing steric interactions within molecules to predict bond dissociation energies of organogermanium compounds using computer models

Introduction

Bond formation represents the foundation of chemistry.[1] By studying the energies associated with bond formation, the relative stability, properties, and possible synthesis reactions of compounds can be predicted. Furthermore, the viability of the compound in various fields of study may be predicted using computational models. Computational chemistry allows for precise simulations of compounds using theoretical models, and removes the need for time intensive physical experimentation.

The proposed experiment intends to examine trends in energy associated with different steric conformations of organogermanium compounds. Determination of trends in bond dissociation energies of the organogermanium compounds will be the primary focus. Bond dissociation energies will be analyzed using a computational approach, as opposed to purchasing germanium to perform a physical experiment. Digermane compounds are not easily purchased from chemical suppliers such as Sigma-Aldrich, hindering physical experimentation. In addition, studying a physical compound doesn't allow for the separating various energy contributions in the compound such as electrical effects or repulsion. The level of methodology associated with the approximations involved in quantum mechanical calculations would be considered, as the higher level, the more accurate the energy approximations according to the Guassian model. Several methyldigermanium compounds will be analyzed using the Gaussian 16 electronic structure program to determine their bond dissociation energies, and the energies associated with seterics.

The success of the research would expand the knowledge about both organogermanium compounds and theoretical-computational technology. Information regarding bond energy and formation would pave the way for additional research regarding the specific mechanisms and interactions undergone by organogermanium compounds. Using a relatively new computer software, Gaussian 16, enables the investigation into the advantages and limitations of the program and how it could be improved for future research purposes, as well as providing a base model set for future studies involving germanium based compounds.

Organogermanium consist of compounds containing carbon–germanium (C–Ge), hydrogen–germanium (H–Ge), or germanium–germanium (Ge–Ge) bonds.[2] Even though there are many different bonds can be formed, the experiment will focus on changes in energies of Ge–Ge bonds as a result of replacing H–Ge bonds with C–Ge bonds. These compounds have various pharmaceutical applications including the production of novel biologically active materials for medical technology. Such products include surgical retention structures, bandages and many products that would contain organogermanium compounds and broad spectrum antibiotics.[3] Organogermanium compounds are also constituents of medicinal plants such as ginseng roots, and are able to contribute to the natural healing properties of ginseng and other natural remedies.[3] This may be attributed to their low toxicity compared to other organic compounds, such as organotin compounds. In addition, organogermanium compounds have applications in the manufacturing of electrical components (i.e. microchips, chip boards, etc.) since they can act as precursors to many different coatings. The experiment will use the

Gaussian 16 modeling software to predict the various energies associated with steric interactions and bond dissociation energy. The software is capable of using principles of quantum mechanics to predict bond dissociation energies, vibrational frequencies, and many other molecular properties of compounds.[4] Gaussian 16 is amongst the most up-to-date softwares and is able to better solve relatively complex calculations as compared to previous computer modeling systems(i.e. Spartan).[4] Importantly, Gaussian 16 can solve the Schrodinger equation which calculates the energy of a chemical system

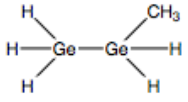
Energies of the bonds between Ge and H, OEt, Br, or Cl have been extensively studied.[5] However, previous research has failed to establish a consistent pattern in the bond energy and formation of Ge-Ge compounds. Specifically there has been minimal investigation into the steric effects of simple substituents on Ge-Ge bond energies. A similar study to our proposed research investigated hexamesityldigermane. Six mesityl groups are present in this molecule with three mesityl on each Ge. Bond dissociation of a Ge-Ge bond is typically 280 ± 21 kj/mol.[6] The bond energy of hexamesityldigermane was determined to be 87 ± 8 kJ/mol.[7] It would appear the the mesityl groups lowered the energy required for the Ge-Ge bond to break through either steric interactions or electron distribution. The intention of the aforementioned study was to compare the energies of hexamesityldigermane to hexamesityldisilicon, not to investigate the direct effects of the substituents on the Ge-Ge bond itself. Our focused study of digermanium compounds will fill the gap in knowledge left by previous research.

Proposed Research

The research project will utilize Gaussian 16 to obtain important information concerning digermane compounds. Gaussian 16 is a relatively new program which is popular and widely-used within the computational chemistry field for investigations into the conceptual aspects of quantum chemistry. In addition to the software itself, a server grade supercomputer which can run Gaussian 16 and efficiently handle the load of multi-computational inputs is required. With the proper hardware, Gaussian 16's capability to simulate the computational chemistry necessary to calculate bond energies, taking into account steric interactions, and convey accurate bond formation information could be utilized.

For the first few months (2-3), the Gaussian 16 computational model program will be optimized for use with germanium based compounds. Optimization will begin with examining previously established silicon models, as silicon has been extensively investigated.[8] Since germanium and silicon are both group 14 elements, they share similar chemical properties. By fine tuning established silicon model, the germanium simulations should provide more accurate results.

(A)



(B)

(C)

(D)

(E)

Figure 1. Various potential compounds that will be studied. (A) digermane, (B) 1-methyldigermane, (C) 1,2-dimethyldigermane, (D) 1,1,2- trimethyldigermane, (E) 1,1,1,2- tetramethylgermane. More compounds will also be studied. These compounds have different methyl group conformations (i.e. 1,1,2,2 - tetramethyldigermane, 1,1,1,2,2,2 hexamethydilgermane, 1,1 - dimethyldigermane, etc.).

In the months thereafter (approximately months 4-18) the various methyldigermaniun compounds (*Figure 1*) will be studied in depth. Each molecule will first be analyzed by virtually constructing the molecule in the Gaussian 16 program. Following this, enthalpy, defined as the thermodynamic energy associated with each molecule, will be calculated through the software. The energies associated with different steric conformations will be quantified by measuring and comparing the energies of each molecule at different rotational conformations. The baseline energy will be represented by the conformation with the lowest energy.

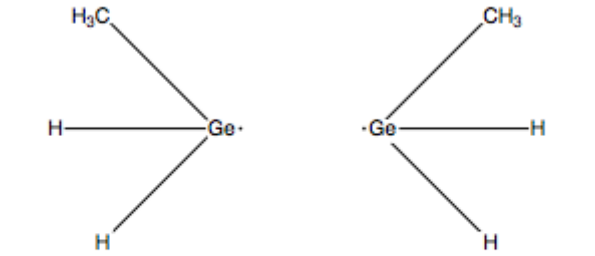


Figure 2. Proposed splitting of methyldigermanium compounds in order to determine bond dissociation energy using the Gaussian 16 software.

The bond dissociation energy of each molecule will be measured by calculating the difference in energy between the compound of interest and the sum of the energies of the two components after the Ge-Ge bond is broken (*Figure 2*). These energies will then be compiled and analyzed in order to determine any possible trends that may have arisen when comparing the different rotational conformations or adding additional methyl groups. After establishing these trends and energies, they will be compared with similar organosilicon compounds to determine any commonalities or discrepancies.

This research is expected to be completed within a 18 month timeline, with monthly evaluation of the effectiveness of the protocol. Should the aforementioned methods fail to render usable results (for instance, if the theoretical computational models exhibit no consistent patterns), alternative strategies would be considered in order to ensure that the project is finished on time. This would include modifications regarding the organogermanium compounds utilized. For instance, instead of analyzing methyl groups, other functional groups such as ethyl or ester groups in organogermanium compounds could be studied via the same software, Gaussian 16.

Germanium has a critical role in modern medicine. For instance, one of its uses is to treat conditions relating to the heart and blood vessels. Examples would be high blood

pressure, high cholesterol, and heart disease. It can also be used to treat glaucoma, cataracts and issues involving the liver; this includes cirrhosis and hepatitis. Some individuals utilize germanium to treat conditions such as rheumatoid arthritis, osteoarthritis, osteoporosis, and even acquired immune deficiency syndrome (AIDS).[9] Success of the research would pave the way for additional medical uses to be investigated, as well as providing a list of viable synthetical compounds.

The results of this experiment would provide information integral to determining the most efficient and energetically favorable way to synthesize organogermanium molecules. By having this information, a more cost effective use of germanium is possible. Would enable future research through physical experimentation. This will be integral to the investigation of additional pharmaceutical applications, thus advancing knowledge in medicine.

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