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Chemistry Honors-in-Discipline Program
East Tennessee State University

Ab Initio Quantum Chemistry Calculations of Phosphorous Oxide Caged Cluster Compounds

Brian Rich

An Honors Thesis submitted in partial fulfillment of the Chemistry Honors-in-Discipline Program, May 2013

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Abstract

Ab Initio Quantum Chemistry Calculations of Phosphorous Oxide Caged Cluster Compounds

The objective of my thesis was to add to a catalogue of molecular structures that is being compiled as a part of the Standoff Detection Project. The optimized geometry of P_8O_{20} and $P_{20}O_{20}$ were calculated using restricted Hartree-Fock Theory, using the standard quantum mechanics and computational chemistry programs ECCÈ and NWChem. Unfortunately, due to the extremely time consuming nature of these calculations there was not enough time to complete the calculations for $P_{24}O_{48}$ and $P_{24}O_{60}$.

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Introduction

The phosphorous oxides comprise a varied and diverse set of inorganic chemistry, particularly the cage compounds.[1-7] The cage compounds have been used as model systems for high-energy laser glasses[8], and as a host material for spent nuclear wastes[9]. They have also been of spectroscopic interest because of the structural similarity to an emerging class of chemical warfare agents.[6-7]

High-quality quantum mechanical calculations are of interest in predicting the vibrational spectra of these compounds, because relatively small changes in structure have been found to lead to significant changes in the vibrational energies[6-7]. This is thought to occur because of the extent to which the formally empty 3d orbitals participate in bonding[10]. The objective of this thesis is to add to the catalogue of phosphorous oxide cage compounds by calculating the optimized geometry. This is an initial step in the calculation of vibrational spectra that may be used for comparison to experimental Raman and IR data.

Quantum Mechanics

Computational chemistry utilizes quantum mechanics to explain how electrons move in a system to influence their surroundings. Quantum mechanics was first explored after Einstein's photoelectric effect supported Planck's formula that showed energy is quantized. Physicists discovered subatomic particles did not behave as classical physics stated they should because of wave-particle duality. This means an electron can move in two ways. An electron can move as an ordinary particle does. In this case classical physics would be able to predict an electron's movement; however, an electron can also move as a wave which threw scientists for a loop.[11] A wave function (Ψ) describes how an electron moves as a wave. This wave function can also be squared (Ψ^2) to find the probability that an electron lies in a certain position. The wave function was introduced to science by the first postulate of quantum mechanics discussed later in the paper.

In 1905 Einstein wrote about the photoelectric effect in a paper and received the Nobel Prize for his work in 1921. Einstein proposed light is a substance made of particle like matter that has energy. This "particle like matter" later became known as photons. Einstein showed that when metal absorbs a photon part of the energy in the photon is used to free the photon from the metal. The rest of the energy that is not used in freeing the photon appears as kinetic energy in an ejected electron.[12] As the light's frequency increases the energy of the photon increases; therefore, there is more energy left in the electron after it escapes the metal. As the intensity of the light increases, while the frequency remains fixed, the number of photons hitting the metal increases; therefore, increasing the rate of emission of electrons. Note the kinetic energy of the electrons is not changed when the intensity of light is increased, but only the number of electrons leaving the metal increases.[13] Einstein's experiment of the photoelectric effect supported Max Planck's work completed in 1900 showing the energy of an electron is proportional to the frequency of radiation and a constant known as "Planck's constant." Both Einstein and Planck were trying to prove a theory that energy is quantized. This means light can only be emitted with certain exact amounts of energy. By proving energy is quantized quantum mechanics was born. Equation 1 shows Max Planck's equation that was supported by Einstein's photoelectric effect.

$$E_{photon} = hv \tag{1}$$

In 1925 Erwin Schrödinger formulated his time-dependent and time-independent Schrödinger equations. The time-dependent Schrödinger is shown in Equation 2.[14]

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{\mathrm{H}} \Psi \tag{2}$$

The time-independent Schrödinger is shown in Equation 3.

$$E\Psi = \hat{\mathrm{H}} \Psi \tag{3}$$

Equation 2 explains how the wave function changes in time and Equation 3 describes a wave function in its stationary state. Both Equations contain the operator $\hat{\mathrm{H}}$ which is the total energy operator and gives the command shown in Equation 4.

$$\hat{\mathrm{H}} = \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(r) \tag{4}$$

The first part to this operator, $\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$, is a calculation of kinetic energy. The second part, V(r), is a calculation of potential energy. Therefore, if kinetic and potential energy of a particle can be found then we will be able to describe the wave function. The wave function that is being described is imperative to how the molecule will form a shape. The first three postulates of quantum mechanics describe why.

Postulates of Quantum Mechanics

Quantum mechanics is a science governed by laws. Since quantum mechanics is occurring at a level we are unable to visibly see we must make all assumptions through use of the postulates. The first postulate tells us we can know the position of any particle based upon its wave function $\Psi(x, y, z, t)$. The first postulate of quantum mechanics states, "The state of a quantum-mechanical system is completely specified by a function $\Psi(x)$ that depends upon the coordinate of the particle. All possible information about the system can be derived from $\Psi(x)$. This function, called the wave function or the state function, has the important property that $\Psi^*(x)\Psi(x)dx$ is the probability that the particle lies in the interval dx, located at the position x.".[15] This postulate states we can know the position of any particle by finding its wave function. The goal of our research is to know the position of each atom (particle) in a compound. The only thing in the way of finding the position of these atoms is discovering the wave functions associated with them.

The second postulate of quantum mechanics states, "To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics."[16] An operator is a command to execute a certain mathematical function on whatever follows it. Operators can be simple or complex. An example of a simple operator is √. When this operator is before a number a command is given to take the square root of whatever is after the operator:

$$\sqrt{9} = 3 \tag{5}$$

The third postulate of quantum mechanics involves finding the wave function for a particle. The wave function can be found by solving the time-dependent Schrödinger equation discussed in Equation 2 above. The time-dependent Schrödinger equation was used in our research to find the wave function of each atom in the molecules being studied. Doing this by hand would have been an extremely arduous task, but most quantum mechanics studies are preformed on the computer. Without computers and computer software our research would not have been possible in the time we did it in. The computer software employed methods such as Hatree-Fock and Density Functional Theory to solve the Schrödinger equation.

Methods of Calculation

Finding kinetic and potential energies for atoms with one or two electrons is not too terribly difficult. Our research involves molecules that contain many electrons. In the case of $P_{24}O_{60}$ there are 1,320 electrons. Each electron is influenced by its kinetic energy, its attraction to the nucleus, and its repulsion from every other electron in the molecule. The Hamiltonian operator for a multiple electron system[13] is shown in Equation 6.

$$\hat{\mathrm{H}} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j<i} \frac{1}{r_{ij}} \quad (in\ atomic\ units) \tag{6}$$

This quickly becomes a math equation that no one is able to solve. In 1928 Hartree introduced the Hartree self-consistent-field (SCF) method. This method uses assumptions to calculate wave functions. If we want to calculate the wave function for the first electron in a system, we must first know the wave function for the first electron, and all the other electrons in the system other than the one for which we are calculating.[17] Essentially you must know the answer to the equation before you solve it (obviously an impossible task). Hartree proposed to solve for the first electron in a many electron system we do not need to know the wave functions of the other electrons, but instead must only guess for the wave functions of the other electrons. This process is known as solving by iteration. We solve for the wave function of the first electron using guesses about the wave functions for the rest of the system. Then use the solution of the first electron's wave function, or total energy operator namely Ĥ, to define the Schrödinger equation for that orbital. This is done for all the electrons in the system until all Schrödinger equations for each orbital are solved. After they are all solved the results are cycled back and used again to recalculate the one electron Hamiltonian operators Ĥ. This iteration is continued until the values for orbitals and energies become consistent from step to step, hence the name self-consistent field method (SCF). Once all values are consistent the total energy for the system is calculated by the expectation value of the many-electron Hamiltonian[18] shown in Equation 7.

$$E_{total} = \langle \Psi | \hat{\mathrm{H}} | \Psi \rangle \tag{7}$$

$$= \langle \Psi \left| -\sum_{i} \frac{\nabla_i^2}{2} - \sum_{i} \frac{Z}{r_i} + \sum_{i} \sum_{j<i} \frac{1}{r_{ij}} \right| \Psi \rangle$$

$$= \langle \Psi \left| \sum_{i} \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + \sum_{j \neq 1} J_j(r_i) \right) + \left[\sum_{i} \left[\sum_{j<i} \frac{1}{r_{ij}} - \sum_{j \neq i} J_j(r_i) \right] \right] \right| \Psi \rangle$$

$$= \sum_i \in_i + \sum_i \left\{ \sum_{j<i} \langle u_i u_j \left| \frac{1}{r_{ij}} \right| u_i u_j \rangle - \sum_{j \neq 1} \langle u_i u_j \left| \frac{1}{r_{ij}} \right| u_i u_j \rangle \right\}$$

The Hartree method does not take the Pauli exclusion principle into account when performing calculations. The Pauli exclusion principle states no two electrons can have identical quantum mechanical states in an atom. This means no two electrons can have matching quantum numbers. A quantum number is a scheme for naming electrons in an atom.[19]

The Hartree-Fock Method is similar to the Hartree Method in that it is also solved by iteration. The Hartree-Fock Method is more accurate because it accounts for something called the Fock operator shown in brackets on the right side of Equation 8. The Fock operator is what takes the Pauli exclusion principle into consideration. Although electrons may occupy the same principal, azimuthal, and magnetic quantum number space they are forced to have separate spins from one another.[20] This is the method we used in our NWChem calculations.

$$\hat{\mathrm{H}} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{j=1}^{N} [2J_j(i) - K_j(i)] \tag{8}$$

The final method of calculation we will discuss is Density Functional Theory (DFT). DFT follows Hohenberg-Kohn (HK) theorem which says the ground-state energy of an atom is directly proportional to the electron density of the molecule[21]. Equation 9 shows the terms used to calculate the total electronic energy (E):

$$E = T + V_{nucl} + V_{rep} + E_{xc} \tag{9}$$

T is the electronic kinetic energy, V_{nucl} is the attraction of the electrons to the nuclei, V_{rep} is the interelectronic coulomb repulsion, and E_{xc} is the exchange correlation energy.

Computational Methods

The first part of this research was to build the molecules of interest in a program called Extensible Computational Chemistry Environment (ECCÈ)[22]. ECCÈ is only used to string together a rough picture of the molecule and what we think it looks like, but the final configuration must be found using calculations given by NWChem. NWChem calculates bond energies within the molecule using Hartree-Fock method (HF) and Density Functional Theory (DFT). The calculations that NWChem performs are used to correct the molecule that was built in ECCE. NWChem will continue to recalculate bond energies until the lowest possible energy configuration is found[23]. The molecules that were chosen for this work are $P_{24}O_{60}$, P_8O_{20}, $P_{24}O_{48}$, and finally $P_{20}O_{20}$.

Calculations based on the fundamental principles of quantum mechanics are referred to as *ab initio* calculations. An *ab initio* study is one in which the entire study is based on theories.[24] In this case the theories that the study is based on are the postulates of quantum mechanics. During this *ab initio* study NWChem is used to calculate potential-energy functions, optimized geometries and; if time had permitted, vibrational frequencies, and Raman and infrared intensities. These values are what allow us to assign a structure to a molecule because we will know what the most stable form of the molecule will be.

Potential-energy functions are calculated by choosing a method and basis set. In our calculations we used the Hartree-Fock method and the 6-31G basis set all potential-energy function calculations. NWChem will run tests on the proposed molecule by changing the distance between two atoms connected by a bond. The distance is measured in Ångstroms while energy is calculated in hartrees. The distance between the two atoms that provides the lowest energy is the most favorable. No matter which method or basis set is chosen for calculations all trials should give the lowest energy possible on the exact same angstrom distance.[25]

Optimized geometries and frequencies are a more realistic picture of what the bonds in the molecule look like because it gives a range for which bond distance is most favorable. Bonds are constantly in motion. The only time any bond would ever stop moving would be if it were to reach 0 kelvin. Because bonds are always, a tolerance is assigned to each bond so that even when they are changing slightly we will still be able to identify the molecule.[26] Multiple methods and base sets will be used in this calculation as no one calculation can be considered 100% correct due to different assumptions made during the calculation (assumptions for each method are discussed later).

The final calculations NWChem is responsible for would be Raman and infrared vibrations. Both Raman and infrared vibrations are used because some bonds are Raman active and infrared inactive; however, other bonds are Raman inactive and infrared active. It is possible for a bond to be both Raman active and infrared inactive, but both values are still measured in case some bonds do not absorb both frequencies. These values are important because all bonds have characteristic absorptions for either Raman or infrared light. They are characteristic to that specific bond type because that bond will only absorb a certain frequency of either Raman or infrared light.[27] Our goal is to know at exactly which frequency of either Raman or infrared light do the bonds in our molecule absorb. If this data is known and recorded then someone will be able to use our catalogue entry of the molecular structures for $P_{24}O_{60}$, P_8O_{20}, $P_{24}O_{48}$, and $P_{20}O_{20}$ to determine if a molecule they found matches our data we recorded. They will be able to compare data for various measurements including potential-energy functions, optimized geometries and frequencies, and finally Raman and infrared intensities.

These molecules were chosen as a part of the Stand-off Detection Project, but because the project is so huge and this is only a small fraction of a finished product there were other reasons these molecules were selected. Clusters of atoms other than carbon are interesting for their use as superconductors and for their storage capacity[28]. There has recently been a lot of attention both experimentally and computationally in the group V elements; nitrogen, phosphorus, arsenic, antimony, and finally bismuth. This is because the caged structures of group V elements are characterized only by single bonds. This means only σ bonds exist within the cage while carbon caged structures contain σ and π bonds within the cage.

Our research attempted to catalogue structures for $P_{24}O_{60}$, $P_{24}O_{48}$, P_8O_{20}, and finally $P_{20}O_{20}$. Unfortunately $P_{24}O_{60}$ and $P_{24}O_{48}$ did not have enough calculation time to complete before the end of the semester so each of those molecules remain unfinished. The nature of solving by iteration takes an extremely long time even when done using computer programs such as NWChem. Even the smaller molecules we studied such as P_8O_{20} took up to two weeks to finish calculating ground state energies. The two molecules that did not finish were larger than the other two so they were not able to be completed. With another semester's worth of time the calculations for $P_{24}O_{60}$ and $P_{24}O_{48}$ should be able to reach completion and their data can be added to the Stand-off Detection Project.

Results

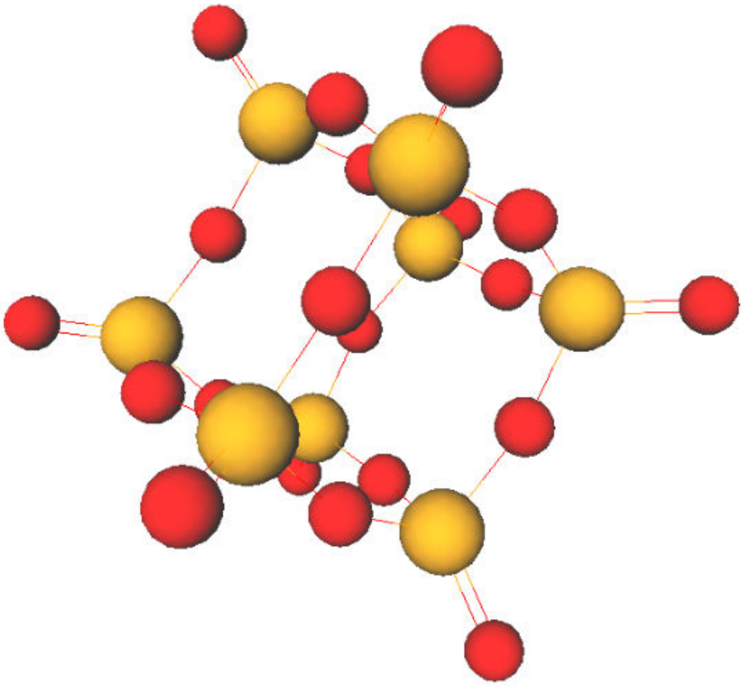

Figure 1: The optimized sturcture of P_8O_{20}.

The first molecule we studied was P_8O_{20}. It was also the smallest molecule we chose to study. Figure 1 shows a picture of P_8O_{20}. This molecule was built in ECCÈ and its optimized geometry was found through Hartree Fock calculations. The values for positions of each atom are reported in Table 1. Each value is reported in units of angstroms.

Table 1: Atom coordinates for the optimized geometry of P_8O_{20}.

Atom Number	Charge	X	Y	Z
1 P	15.0000	2.78433346	0.16061306	0.26880368
2 O	8.0000	2.02574160	-1.26657774	0.57276918
3 P	15.0000	1.04892445	-2.57280985	0.36248198
4 O	8.0000	-0.18270385	-2.15742998	1.37017014
5 P	15.0000	-1.11435103	-1.16083952	2.28737468
6 O	8.0000	-0.21453972	0.20971414	2.14200587
7 P	15.0000	0.64616640	1.61187636	2.19228775
8 O	8.0000	1.91571957	1.14714075	1.25717271
9 O	8.0000	1.66544827	-3.97726217	0.51126592
10 O	8.0000	-1.52348936	-1.63205583	3.69659858
11 O	8.0000	0.94120429	2.25032060	3.56367378
12 O	8.0000	4.32151152	0.20600511	0.36756114
13 O	8.0000	2.08718705	0.53002130	-1.17229469
14 P	15.0000	1.08244126	1.15260111	-2.31284433
15 O	8.0000	0.02302901	-0.09867181	-2.44639114
16 P	15.0000	-0.65313587	-1.58080181	-2.21896166
17 O	8.0000	0.37361118	-2.16981586	-1.08004756
18 O	8.0000	0.18891581	2.16324137	-1.37136702
19 P	15.0000	-1.01757749	2.58132381	-0.33614804
20 O	8.0000	-0.22355498	2.49407490	1.10550420
21 O	8.0000	-1.80384163	1.13570232	-0.28743882
22 P	15.0000	-2.77781251	-0.19081902	-0.24089811
23 O	8.0000	-2.31677101	-0.80135711	1.21898997
24 O	8.0000	-1.91785073	-1.15552982	-1.25670701
25 O	8.0000	1.70608011	1.72241926	-3.60170817
26 O	8.0000	-1.83142481	3.85597231	-0.63330979
27 O	8.0000	-4.28607036	-0.00981277	-0.50134187
28 O	8.0000	-0.94367744	-2.44963550	-3.45811223

The second molecule studied was $P_{20}O_{20}$. This molecule is quite a bit bigger and as a result took longer to perform calculations on. This was the largest molecule we were able to complete calculations for. This is a result of solving by iteration. The process of guessing values and reguessing after solving takes a very long time. One semester was not enough time to perform Hartree-Fock calculations on $P_{24}O_{48}$ and $P_{24}O_{60}$. Figure 2 shows a picture of the optimized geometry for $P_{20}O_{20}$.

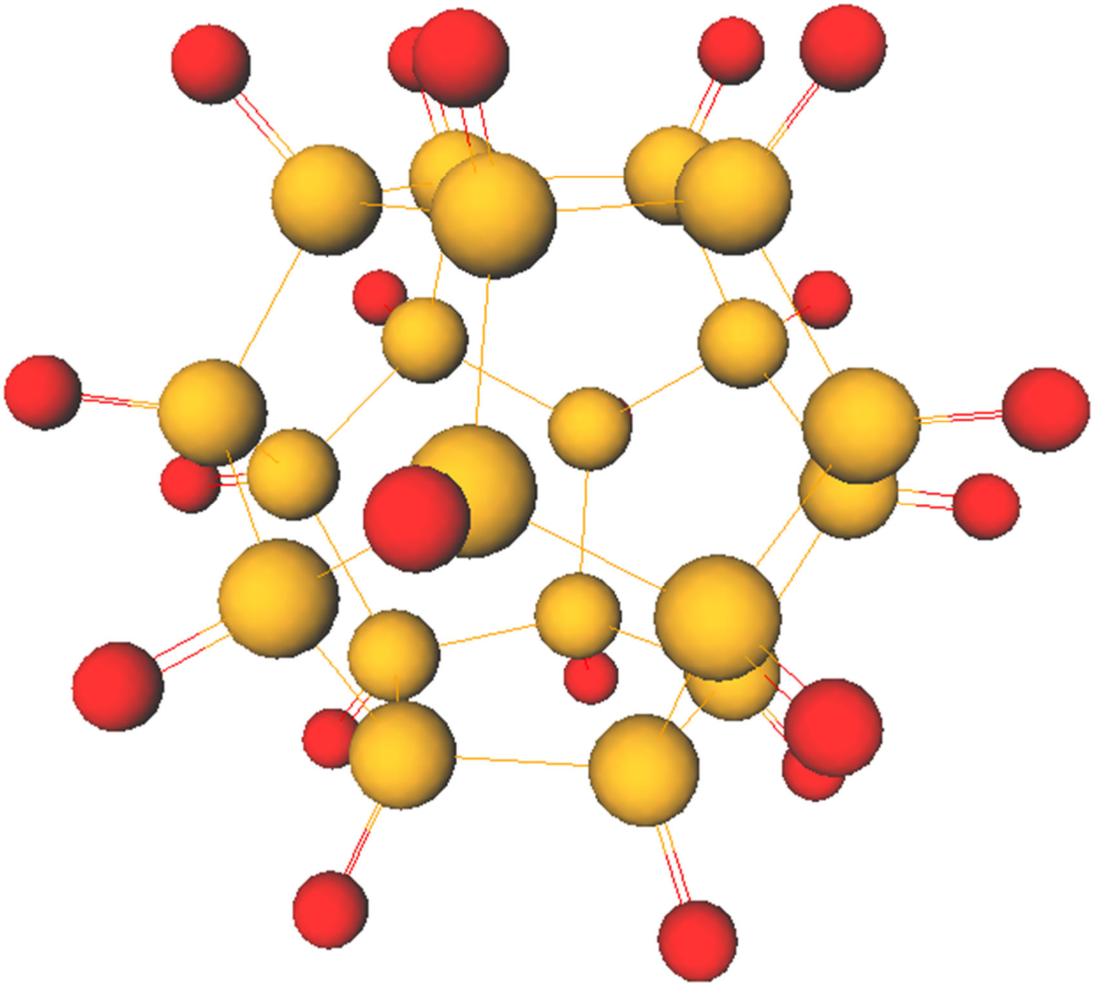

Figure 2: The optimized sturcture of $P_{20}O_{20}$.

The values for positions of atoms in $P_{20}O_{20}$ are reported in Table 2. All values are reported in units of angstroms.

Table 1: Atom coordinates for the optimized geometry of $P_{20}O_{20}$.

Atom Number	**Charge**	**X**	**Y**	**Z**
1 P	15.0000	2.34958373	-2.33660339	0.04523601
2 P	15.0000	1.36102658	-2.09157962	2.18033106
3 P	15.0000	1.65317110	0.15132531	2.86960972
4 P	15.0000	2.82175057	1.29325157	1.15983518
5 P	15.0000	3.25301886	-0.24404034	0.58588668
6 O	8.0000	3.47761351	-3.45914538	0.06910661
7 O	8.0000	4.81537685	-0.36165690	0.86585673
8 O	8.0000	4.17710081	1.91579274	1.71536329
9 O	8.0000	2.44607021	0.22299898	4.24780740
10 O	8.0000	2.01478888	-3.09729069	3.22630357
11 P	15.0000	2.10221946	0.49844468	2.51408693
12 P	15.0000	1.40406661	2.9858245	0.30872614
13 P	15.0000	0.96004992	2.49379873	-1.96176205
14 O	8.0000	3.10992108	0.73472759	-3.72306044
15 O	8.0000	1.41809033	3.69180286	-2.90412255
16 O	8.0000	2.07967520	4.41911164	0.45840169
17 P	15.0000	0.64085995	-2.88894145	-1.49293561
18 P	15.0000	0.48623667	-1.13723171	-3.07458018
19 O	8.0000	0.72186447	-1.68277642	-4.55095380
20 O	8.0000	0.94913222	-4.27553990	-2.21092781
21 P	15.0000	-0.96004992	-2.49379873	1.96176205
22 P	15.0000	-1.40406661	-2.98582455	-0.30872614
23 O	8.0000	-2.07967520	-4.41911164	-0.45840169
24 O	8.0000	-1.41809033	-3.69180286	2.90412255
25 P	15.0000	-0.48623667	1.13723171	3.07458018
26 P	15.0000	-0.64085995	2.88894145	1.49293561
27 O	8.0000	-0.94913222	4.27553990	2.21092781
28 O	8.0000	-0.72186447	1.68277642	4.55095380
29 P	15.0000	-2.10221946	-0.49844468	2.51408693
30 O	8.0000	-3.10992108	-0.73472759	3.72306044
31 P	15.0000	-1.65317110	-0.15132531	-2.86960972
32 P	15.0000	-1.36102658	2.09157962	-2.18033106
33 O	8.0000	-2.01478888	3.09729069	-3.22630357
34 O	8.0000	-2.44607021	-0.22299898	-4.24780740
35 P	15.0000	-2.34958373	2.33660339	-0.04523601
36 O	8.0000	-3.47761351	3.45914538	-0.06910661
37 P	15.0000	-3.25301886	0.24404034	0.58588668
38 O	8.0000	-4.81537685	0.36165690	0.86585673
39 P	15.0000	-2.82175057	-1.29325157	-1.15983518

40 O	8.0000	-4.17710081	-1.91579274	-1.71536329

Future Work

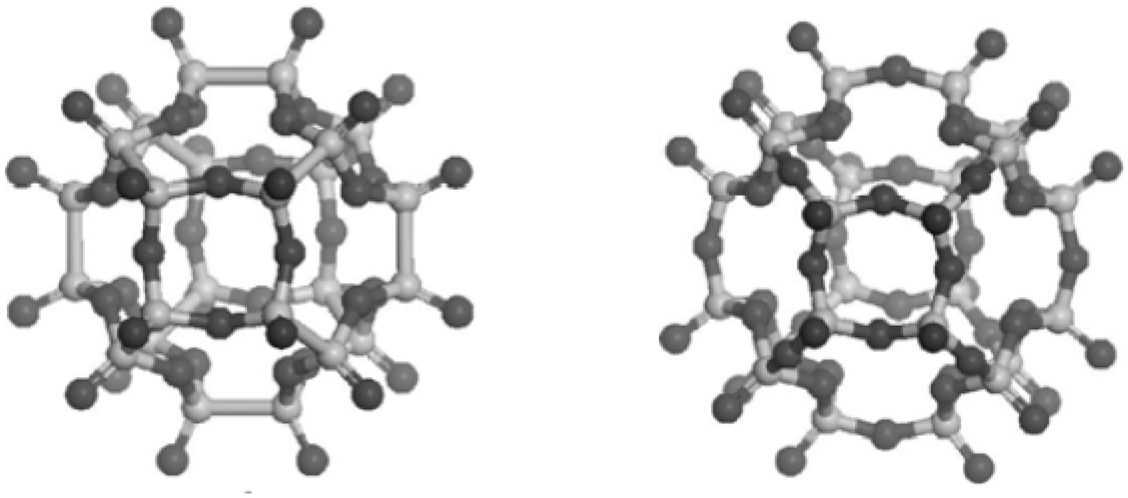

Figure 3: The hypothesized sturctures of $P_{24}O_{48}$ and $P_{24}O_{60}$.

In future work, the molecules $P_{24}O_{48}$ and $P_{24}O_{60}$ should have their optimized geometry calculations finished. Both of their structures have been built in ecce so only computational time needs to be invested. Figure 3 shows proposed structures for $P_{24}O_{48}$[28] and $P_{24}O_{60}$.[28]

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