

Density functional theory simulations of molecules

Introduction

The aim of the task was to investigate the Diazene (N_2H_2) and $P(OH)_5$ molecules and to analyse the changes occurring to their structures when the number of electrons surrounding them also changes. Density Functional Theory (DFT) simulations were used in a bid to study the behavior of the molecules; DFT allows understanding the quantum mechanical effects experienced by materials due to the presence of electrons. Figure 1 shows the cis- form of the diazene molecule and the $P(OH)_5$ molecule.

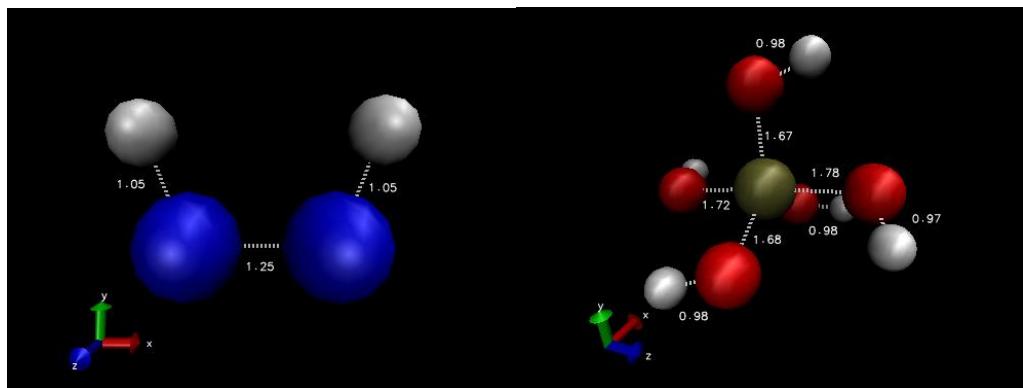


Figure 1: Cis form of Diazene (N_2H_2) and $P(OH)_5$ molecules. Blue spheres represent nitrogen atoms, white spheres represent hydrogen atoms, red spheres represent oxygen atoms and gold spheres represent phosphorous atoms

Diazene can be used as a reagent in organic synthesis because it selectively reduces alkenes; it is also nonreactive when exposed to many functional groups. Diazene can exist as two stereoisomers, Cis (the Z form, with polar pairs on the same side) and Trans (the E form, with polar pairs on opposite sides). The double bond between the two nitrogen atoms provides structural rigidity to the molecule and on each nitrogen atom is a lone pair of electrons, these are valence electrons not shared with a neighbouring atom as shown in figure 2:

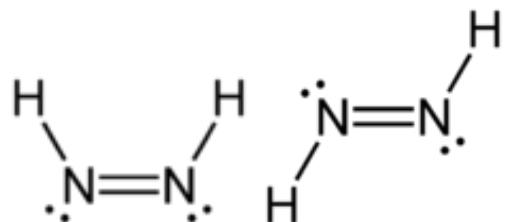


Figure 2: The cis- and trans- stereoisomers of Diazene, lone pairs are denoted by the double dots

With the hydrogen atoms being present on the same side of the molecule, there is the chance of steric clashes occurring, since there is one electron on each hydrogen atom, this effect is small but still present. DFT simulations were used to model these structures.

DFT code

When the Schrödinger equation is solved exactly for a particular system, its wavefunction can be obtained. From this the allowed energy states of the system can be determined. However, for an N-body problem the Schrödinger equation becomes very difficult to solve and approximations must be used to simplify the problem.

One such approximation involves using DFT which can be thought of as a method to obtain an approximate solution to the Schrödinger equation when looking at many-body systems. In this set of simulations, DFT codes were used to investigate the structural properties of diazene and P(OH)₅. The code used was the Car-Parrinello Molecular Dynamics code (CPMD), one of its many features includes being able to move electrons and atoms simultaneously when performing molecular dynamics. The input file contains the necessary instructions for the CPMD code to be run, these input scripts are shown in table 1.

Table 1: The input scripts used in the input files

&SECTIONNAME	Description
&CPMD	These are the general control parameters needed for the calculation
&DFT	Exchange and correlation functional and related parameters
&SYSTEM	Simulation cell and plane wave parameters
&ATOMS	Atoms and pseudopotentials and related parameters

The code essentially utilises the Klenmar-Bylander pseudopotentials in the section denoted as &ATOMS to decrease the computational time required for the simulation to occur as it scales linearly with the basis set. The geometry optimizations carried out are repeated single point calculations in which the atomic positions are updated according to which forces act on them. The input file is divided into sections starting with &NAME and ending with &END, text which is outside of these sections is not taken into account, care must be taken in writing the sections in capital letters or else they will be ignored, all input files are required to have &CPMD, &SYSTEM and &ATOMS sections.

The output file contains a list of xyz coordinates which pinpoint the position of the two nitrogen and hydrogen atoms in the molecule over step number, from this coordinate file it will be possible to use VMD to measure the change in bond length and angle. The CPMD code differs from the Optimised Potentials for Liquid Systems (OPLS) force field code in that the OPLS code makes all the interaction sites centre on the atoms, and does not take into account lone pairs of electrons. OPLS code is best suited to study liquid properties including density and heat of vaporization. The CPMD code is capable of modelling electrons, a feature which is not available when using OPLS code.

Simulations

The geometry optimisation simulation for the neutral stereoisomers of Diazene was carried out and the same structures as those seen in figure 2 were obtained as seen in figure 3 below:

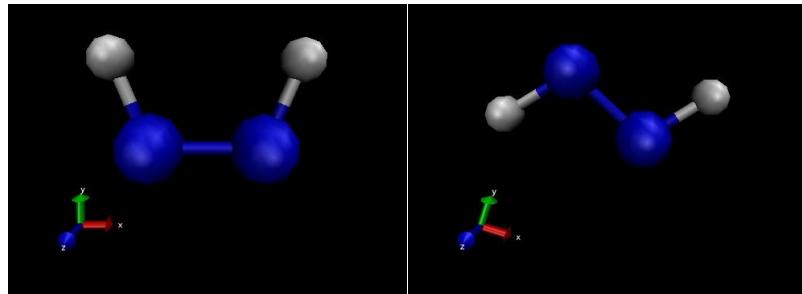


Figure 3: The Cis- and Trans- stereoisomers occurring after optimisation of the neutral Diazene molecule

Once the GEO_OPT trajectory file has been created for both the neutral and ionised stereoisomers, important information regarding the molecule can be obtained such as bond length, bond angle, dihedral angle and the final energies of the cis- and trans- configurations as can be seen in table 2:

Table 2: Average bond length, bond angle, dihedral angle and final energy for each neutral N₂H₂ species. In brackets are the equilibrium values found with the OPLS force field code.

Species	Average Bond Length (Angstroms)	Average Bond Angle (Degrees)	Average Dihedral Angle (Degrees)	Final energy (eV)
Cis	N-H (1.01) 1.05	N-N (1.45) 1.25	N-N-H (118.4) 112.10	H-N-N-H 0.07
				-570.41
Trans	1.04	1.25	106.68	180.00 -570.62

The average bond lengths for the neutral cis- and trans- isomers differ by 0.01Å for the N-H bond and are roughly the same for the N-N bond. The difference between the N-H bond length averaged over the cis- and trans- stereoisomers and the equilibrium value found within the OPLS force field code is of 0.03Å. The difference between the N-N bond length averaged over the cis- and trans- stereoisomers and the equilibrium value found when calculated with the OPLS force field code is of 0.20Å. The difference in the N-N-H bond angle between the cis- and trans- isomers is 6.42° whereas the difference between the equilibrium bond angle and the N-N-H bond angle averaged over the cis- and trans- isomers is 9.01°. The final energies of the neutral diazene molecule are roughly the same, differing by 0.21eV, mainly due to steric clashes, which allow the trans- configuration to be slightly more energetically favourable than the cis- configuration.

The energy in the OPLS forcefield is given by equation 1 below:

$$E(r^N) = E_{bonds} + E_{angles} + E_{dihedrals} + E_{nonbonded} \quad (1)$$

Where the individual components are given by:

$$E_{bonds} = \sum_{bonds} K_r(r - r_0)^2 \quad (2)$$

$$E_{angles} = \sum_{angles} K_\theta (\theta - \theta_0)^2 \quad (3)$$

$$E_{dihedrals} = \frac{1}{2} V_1 [1 + \cos(\varphi)] + \frac{1}{2} V_2 [1 - \cos(2\varphi)] + \frac{1}{2} V_3 [1 + \cos(3\varphi)] + \frac{1}{2} V_4 [1 - \cos(4\varphi)] \quad (4)$$

$$E_{nonbonded} = 0 \quad (5)$$

Where $K_r(N-N)=350\text{kcal/mol}$, $K_r(N-H)=434\text{kcal/mol}$, $K_\theta(N-N-H)=56\text{kcal/mol}$ and $V_i=V_2=V_4=0$ and $V_3=0.3\text{kcal/mol}$. E_{bonds} represents the energy of the covalently bonded atoms, the harmonic oscillator approximation becomes less and less reliable the larger the bond length. E_{angle} represents the energy due to the geometry of the orbitals involved in covalent bonding, it derives from Hooke's law. $E_{dihedrals}$ represents the energy for twisting a bond. $E_{nonbonded}$ are only counted for atoms three or more bonds apart, since the diazene molecule is very small, $E_{nonbonded}$ is therefore equal to 0 for diazene. The value for r and r_o is given in Angstroms, the value for θ and θ_o is given in degrees as is the value for φ .

The value of the constants k_r and k_θ can be determined quantum mechanically via the use of the QMIDFF generation algorithm. After the potential functions have been assigned and topological analysis has been carried out, the algorithm proceeds by calculating the previously unknown values of k_r and k_θ . The Levenberg-Marqardt (LM) algorithm minimizes the squared deviations between the quantum mechanical and force field Hessians.

The dihedral potential is not fully understood, however, repulsive interactions between bond orbitals which overlap and the occurrence of steric clashes between atoms contribute to such a potential. When looking at the functional form for the H-N-N-H species, the minimum energy occurs when:

$$\frac{dE}{d\varphi} = -\frac{3}{2} V_3 [\sin(3\varphi)] = 0 \quad (6)$$

The values of φ which make this so are: 0° , 60° , 120° and 180° . The dihedral angle which is equal to 0° corresponds to the cis- stereoisomer, whereas the one corresponding to 180° corresponds to the trans- stereoisomer. The 60° and 120° values correspond to the eclipsed and staggered configurations of the molecule. When substituting these values of φ in the OPLS forcefield code the minimum energy for both the cis- and trans- configurations was respectively found as being 0.13eV and 0eV . From this data it would seem that the trans- configuration is more energetically favourable than the cis- configuration for the neutral atom, however, more information is required to confirm this statement. It is impossible to perform a direct comparison between the final energies of the OPLS forcefield code and that calculated using CPMD as the values for r and θ are missing from the data gathered, hence, if conclusions have to be drawn from the data available, and assuming that the total energy calculated by using the OPLS code follows the same trend as the dihedral energy, it would result in the total energy of the neutral cis- species being smaller than that of the neutral trans- species, this is not in agreement with what is observed in table 2.

Overall, the OPLS forcefield code does a relatively good job in simulating the neutral diazene molecule; the bond lengths found with CPMD code do not differ by more than 3% with the equilibrium values calculated via OPLS however, the OPLS forcefield does not fully take the into account the repulsion force of the lone pair of electrons, resulting in the N-N-H angle being much larger for the OPLS calculations than for that found in CPMD.

Ionised Diazene

The geometry configuration optimisation simulation of the cis- and trans- N_2H_2 molecule after the removal of two electrons, was also carried out. The ionisation made the molecule have a net charge of +2, such a process is endothermic as the input of ionization energy is required, this can be seen when comparing table 2 with table 3 below, the final energy of the system is higher for the ionised species than for the neutral species. The number of valence electrons in the neutral diazene molecule is twelve as the two nitrogen atoms each possess five electrons in their outer shell whereas the hydrogen atoms have one valence electron each, this leaves an electron cloud on each of the two nitrogen atoms for both the cis- and trans- stereoisomers. Once the ionization occurs, the number of valence electrons decreases to ten.

The code used for the molecular dynamics calculation is of the same format as that used to model the behaviour of the neutral diazene molecule, however, there is the addition of the MAXSTEP and TIMESTEP in the &CPMD section as well as CHARGE +2.0 in the &SYSTEM section which corresponds to the ionisation being carried out. The average bond length, bond angle and dihedral angle for the cis- and trans- stereoisomers was analysed with VMD to understand what changes occur in the diazene molecule when it is ionized and are listed in table 3:

Table 3: Average bond length, bond angle, dihedral angle and final energy for each ionized N_2H_2 species. In brackets are the OPLS equilibrium values

Species	Average Bond Length (Angstroms)		Average Bond Angle (Degrees)	Average Dihedral Angle (Degrees)	Final energy (eV)
	N-H (1.01)	N-N (1.45)	N-N-H (118.4)	H-N-N-H	
Cis+2	1.11	1.09	179.93	0.54	-543.49
Trans+2	1.11	1.09	179.88	177.25	-543.48

The two final energies are very similar, indicating that the final molecular configuration of the cis- and trans- molecules must also be very similar. When snapshots of the trajectory were taken, it became clear that the stereoisomers of the diazene molecule were changing shape:

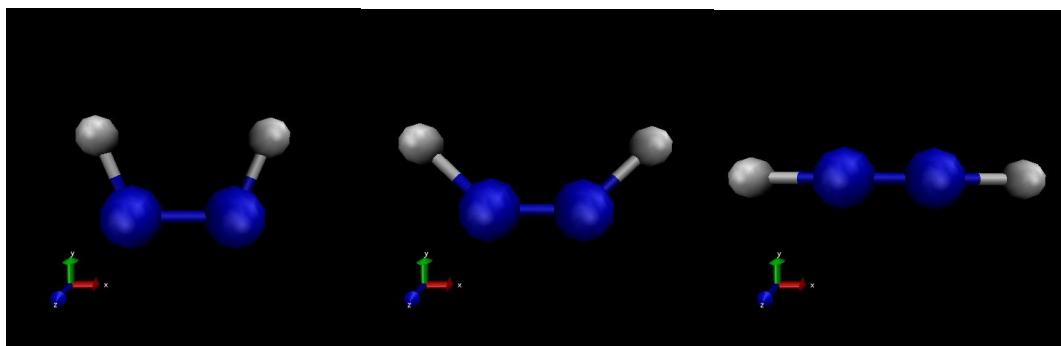


Figure 4: The change in shape of the Cis- N_2H_2 molecule over the course of geometry optimisation

In the trajectory for the Cis+2- N_2H_2 molecule the angular separation between the hydrogen atoms increases, they are pushed further and further from each other until the angular separation is 180° . When looking at the Lewis dot diagram in figure 2 it can be seen how each nitrogen atom possesses a lone pair of electrons, a lone pair is very electronegative and these will repel each other as much as

possible to maximise the distance between them. In order to maximise repulsion, they exert a force also on the hydrogen atoms such that these are at the maximum possible distance from the lone pair as well, however, when an electron is removed, the repulsion force from these electron clouds decreases, and hence the separation between the hydrogen atoms increases, as they are being pushed together with lower force.

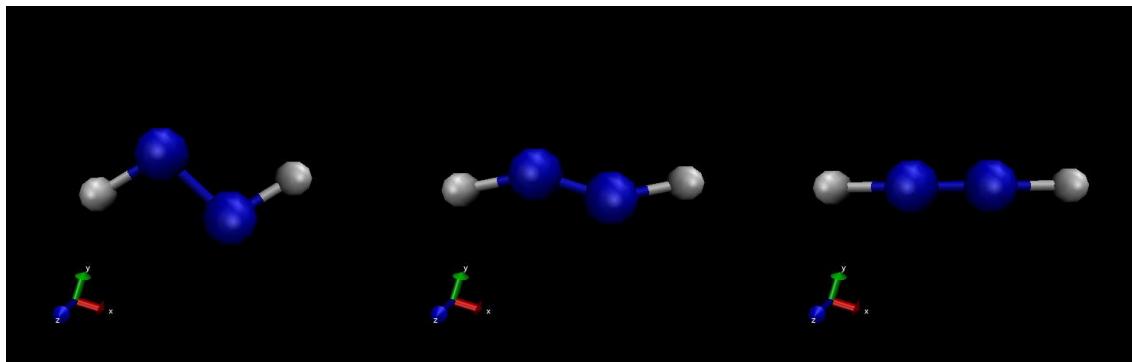


Figure 5: The change in trajectory of the Trans- N_2H_2 molecule over the course of geometry optimisation

In the trajectory for the Trans+2- N_2H_2 molecule, a similar process occurs, with the lone pairs losing an electron each and the hydrogen atoms being repelled with smaller force by the free valence electrons found on the nitrogen atoms, thus feeling greater repulsion from the other hydrogen atom.

However, if in both the cis- and trans- configurations, an unbound electron was still to be on each nitrogen atom, the final structure would not look linear, but trigonal planar. When removing one electron from each of the nitrogen atoms, a free radical is formed, these are species which possess an odd number of electrons, and they are extremely reactive and short lived as they want to take an electron from other atoms in order to become stable. In the case of diazene, the two free radicals will form a triple bond between the nitrogen atoms as each tries to have a full octet. The resulting structure is therefore linear and not trigonal planar. This conclusion is further confirmed by looking at the length of the bonds in the initial and final configuration of each ionised stereoisomer. From table 2 it can be seen how the bond length for the ionised cis- and trans- configurations is equal to 1.11 Å, according to literature, the length of the N-N triple bond is 1.10 Å. The length of the N-N double bond is given by literature as being 1.24 Å, matching very closely to the values in table 2 for the cis- and trans- configurations, respectively 1.29 Å and 1.25 Å.

When comparing the neutral diazene with the ionized diazene, expected changes in bond angles, bond length, dihedral angle and final system energy occur. The N-N bond length of both the cis- and trans- species decreases when these species are ionised, this is because a triple bond is formed between the two nitrogen atoms in the ionised case, hence the atoms will be pulled together with greater force, resulting in a shorter bond. The N-N-H bond angle goes from depicting an asymmetric (due to the lone pairs exerting more force than the hydrogen atoms' electron clouds) trigonal planar configuration to a linear one, this is because there are no more lone pairs in the ionised structure of diazene, hence the hydrogen atoms can maximise their repulsion and be at 180° to each other.

There is close to no change in the dihedral angle because the molecule changes shape in a symmetrical fashion; the H-N-N angle undergoes the same angular change as the N-N-H angle resulting in an overall change in dihedral angle equal to 0, there is no twisting occurring around the double (now turned triple bond) essentially due to the fact that twisting can only occur between

atoms joined together by a single bond, as an sp and sp² hybridized atom does not allow twisting. Since an endothermic reaction has occurred, it comes as no surprise that the final energy of the ionised stereoisomers is higher than that of the neutral stereoisomers.

Discrepancies also arise when comparing the value for bond lengths and angles when utilising CPMD code with the corresponding equilibrium values calculated with the OPLS force field. The N-H bond for the Cis+2 and Trans+2 configurations is found to be 0.10Å larger when calculated via the OPLS force field code than when calculated with the CPMD code, and the N-N bond for the Cis+2 and Trans+2 configurations is found to be 0.36Å larger when calculated using the CPMD code than with the OPLS force field code. The N-N-H angle is very different for the optimised diazene CPMD simulation compared to the equilibrium angle calculated with the OPLS code, this is because in the OPLS classical simulation the molecule has not been recognised as undergoing a structural change.

These differences are expected as the CPMD takes into account the quantum mechanical behaviour of the atoms, whereas the OPLS forcefield gives a classical interpretation of the system, and most importantly, does not take into account the effect of the lone pairs of electrons found on the nitrogen atoms; this results in the simulation not being able to pick up the formation of the triple bond which has been simulated by the CPMD code. The OPLS classical forcefield does not capture the behaviour of the ionised diazene molecule observed in the CPMD calculations.

POH₅

As in the case of the Diazene molecule, two simulations were run on the POH₅ species. The first involved carrying out geometry optimization of the neutral P(OH)₅ molecule. The optimized structure is shown below:

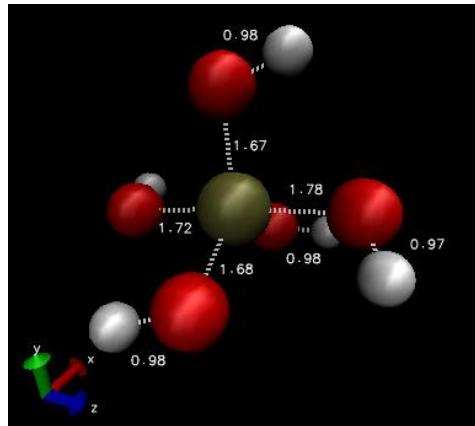


Figure 6: Optimised structure of P(OH)₅; the red spheres represent oxygen atoms, the white spheres represent oxygen atoms and the golden central atom represents the phosphorous atom

The structure clearly shows that the OH groups are trying to maximize their separation from each other resulting in a trigonal bipyramidal structure (more noticeable if figure 5 is looked at sideways). This can be confirmed by the use of VSEPR theory; the number of valence electrons of the P(OH)₅ molecule is 40, this leads to a coordination number of 5 for the central phosphorous atom, which

forms single bonds with the oxygen atoms. These oxygen atoms will possess two lone pairs of electrons pushing the hydrogen atom which is also bonded to the oxygen.

As in the diazene case, the repulsion from the lone pair of electrons is larger than that of the hydrogen cloud, resulting in an expected P-O-H bond angle being lower than 120° . The evolution of the normalized average values for the energy of the system, the O-H and P-O bond lengths, and the O-P-O and P-O-H bond angles over step size is shown in figure 7:

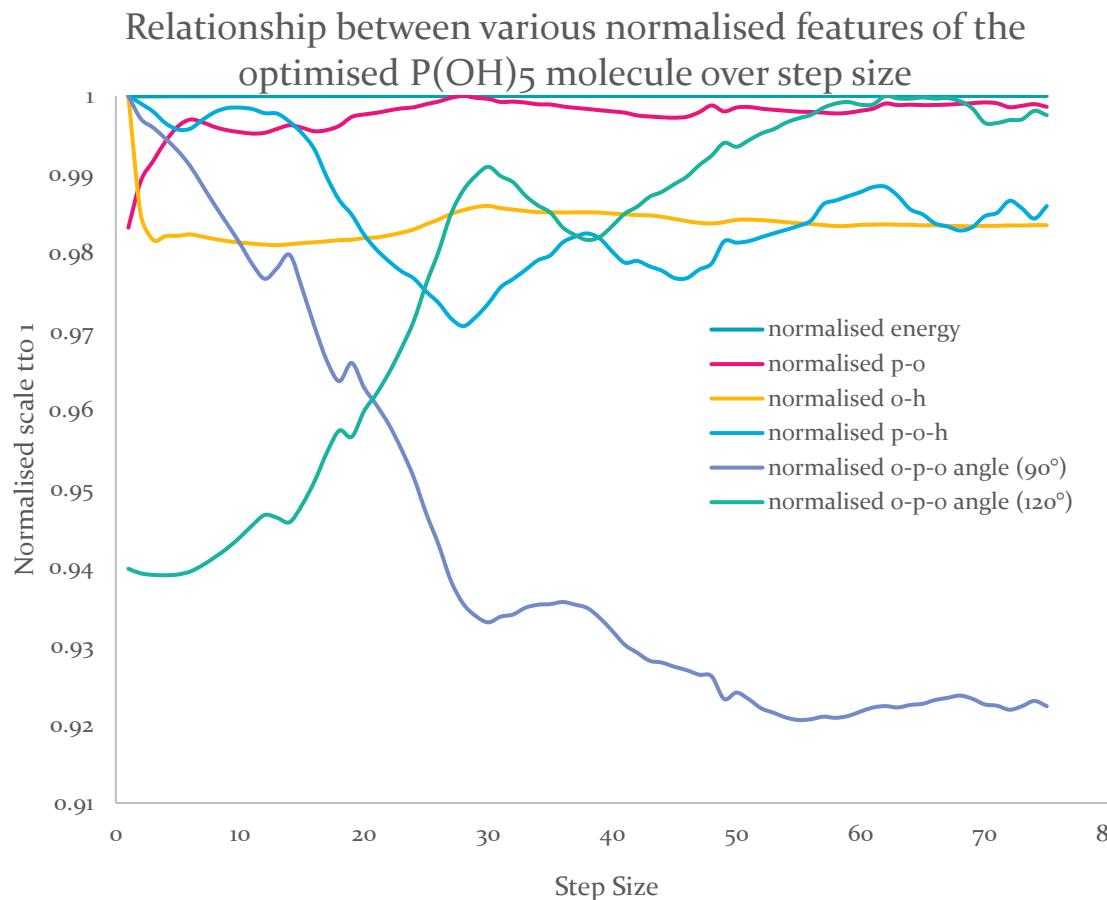


Figure 7: Relationship between normalized average energy, average P-O and O-H bond length, and average P-O-H and O-P-O bond angles over step size.

As can be seen from the graph, the variation in step size of the average O-H and P-O bond is relatively small, with both bonds varying by no more than 0.5% throughout the simulation after step 3. The change in the average P-O-H angle however is quite noticeable reaching a maximum percentage variation equal to 3% at step 28. The most interesting correlation however is between the average OPO angles corresponding to the two values oscillating around 90° (dark green) and 120° (dark blue). It can be seen how the increases in one angle lead to a quasi-equal decrease in the other one and vice versa. This is even more noticeable if a mirror line is drawn parallel to the x-axis at point (20, 0.96) the near specular nature of the lines is clear. From figure 7 the relationship with which the energy of the system changes with step size is deceptive, the change in energy of the system over step size is shown in figure 8:

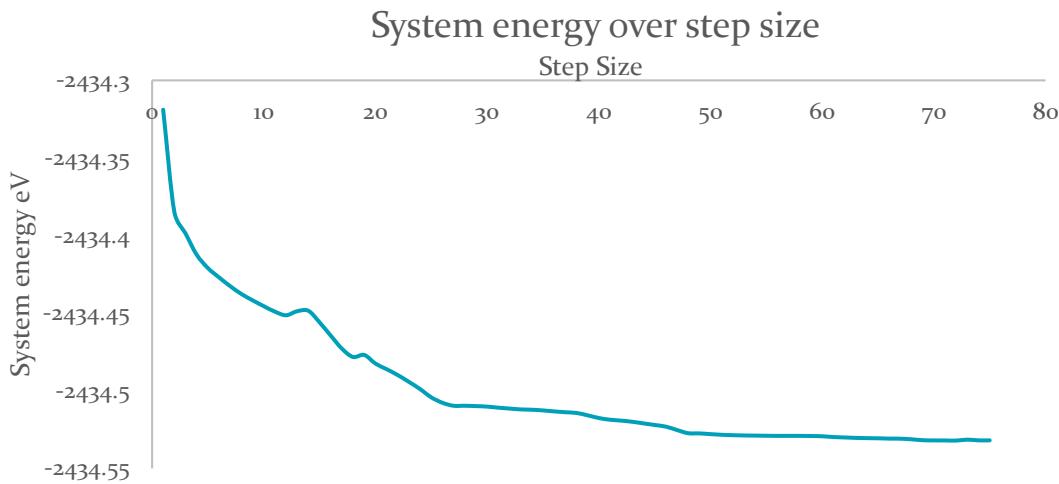


Figure 8: The decrease in energy of the system follows an exponential decay curve

As can be seen from figure 8, the energy of the system decreases exponentially with respect to step size; the rate of change of energy is fastest at the start of the simulation and as it approaches the optimized state the rate of increase tends to zero, this can be explained in terms of the exponential nature of the equilibrium rate constant, which states that in a reaction:



the ratio of the populations of A and B at equilibrium (respectively A_{eq} and B_{eq}) is given by:

$$\frac{B_{eq}}{A_{eq}} = K = e^{\frac{-\Delta G}{k_B T}} \quad (8)$$

where K is the rate constant, k_B is the Boltzmann constant, T is the temperature of the system and ΔG is the change in the Gibbs Free energy of the system. It can be seen how the exponential nature of the graph in figure 8 relates to this fundamental property of solutions which strive to achieve equilibrium.

Table 4: Average bond length, bond angle, dihedral angle and final energy for the POH_5 species found when using CPMD. In brackets are the equilibrium values found within the OPLS force field.

Species	Average Bond Length (Angstroms)		Average Bond Angle (Degrees)		Average Dihedral Angle (Degrees)	Final energy (eV)
P(OH)_5	P-O (1.61) 1.67	O-H (0.945) 0.982	O-P-O ¹ (102.6°) 100.2	P-O-H (108.5) 109.2	O-P-O-H 26	-2434.53

From table 4 it can be seen how the difference between the average P-O bond lengths and the equilibrium P-O bond lengths is 0.06 Å and that between the average O-H bond lengths and the

¹ This angle has not taken the 180° O-P-O bond into account, resulting in a value closer to the equilibrium value.

equilibrium O-H bond length is 0.037 Å. The difference between the average O-P-O angle and the equilibrium O-P-O angle is 2.4°. It is expected that the average dihedral angle is 26°, if all the dihedrals were to cancel each other out the average dihedral angle should be 0°, however there is a dihedral of 120° which contributes to the average dihedral angle which does not cancel with another dihedral. Hydrogen bonding occurs in the molecule as the hydrogen atoms are bonded to the oxygen atoms, hydrogen bonding generally occurs between the hydrogen atom and nitrogen, oxygen and fluorine species due to their high electronegativity.

Molecular Dynamics simulation of the P(O₅H₄)- anion

The code used for this simulation is similar to the one used for the ionised diazene simulation; in the &CPMD section, the initial temperature was set to 300K, and in the &SYSTEM section the charge of the molecule was set to -1.0, information regarding the phosphorous, oxygen and hydrogen atoms was added in the &ATOMS section.

When a hydrogen atom is removed from P(O₅H₅) it turns into monoionic phosphorane, which possesses a negative charge. A noticeable structural change occurs, in which a water molecule is formed:

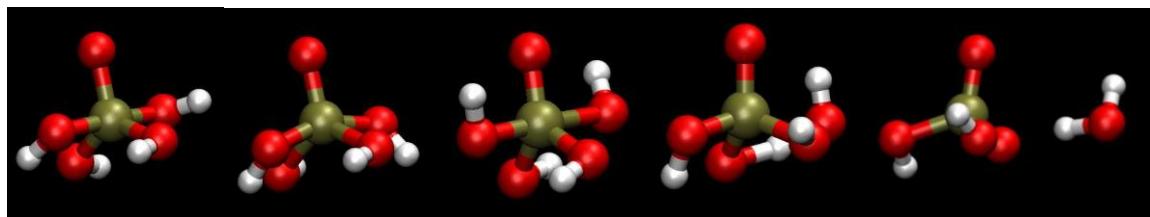


Figure 9: P(O₅H₄)- anion undergoing a structural change, from left to right, snapshots taken at step 1, step 211, step 500, step 977 and step 1200.

To go from pentacoordinated phosphorous P(OH₅) to monoanionic phosphorane P(O₅H₄)⁻ a series of key steps are needed; firstly, at step 933 one of the P-O bond lengths increases to 2.19 Å and the corresponding dihedral angle for the OPOH group is -11.01°, at this point, the OH group splits from the phosphorous central atom group. At step 952 the OH group finds itself at a minimum distance of 1.50 Å from a neighbouring OH group, the free OH group is rotated with the negative oxygen head pointing towards the positive hydrogen atom, which belongs to the OH group bonded to the phosphorous, and forms a hydrogen bond with it.

The length of the O-H hydrogen bond is stretched to 1.48 Å in the process, since this is much larger than the hydrogen bond occurring in the initial structure where it was 0.982 Å, it is less strong. In bonding with the hydrogen atom this new OH group has stretched the OH bond of the species bonded to the phosphorous, until when at frame 1000 the bond is so weak that it allows a water molecule to break off entirely.

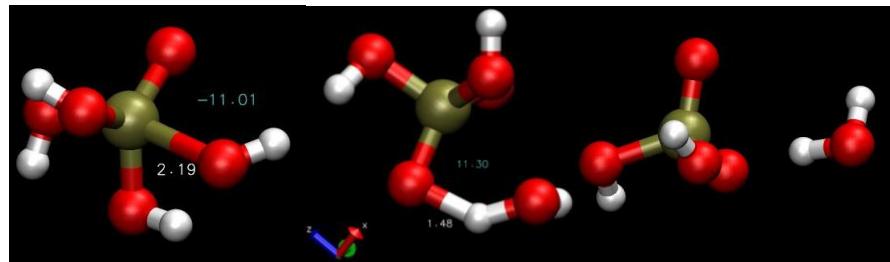


Figure 10: At step 933, OH group breaks off, at step 952, the OH group bonds to a neighboring OH group, at step 1000 H₂O breaks off

Between steps 950 and 1000 multiple bond breakages and subsequent formations were visible on VMD, care must be taken in interpreting these as in reality the molecule does not undergo multiple bond formation and breakage, this visual misrepresentation is solely caused by the cutoff distance in the GRAPHICAL REPRESENTATIONS command window where a bond will be shown to form between atoms separated by a distance lower than the value inputted. The default cutoff distance used was of 1.5Å. The structural changes occurring can also be visualized when plotting a graph of energy vs step size and temperature vs step size of the system:

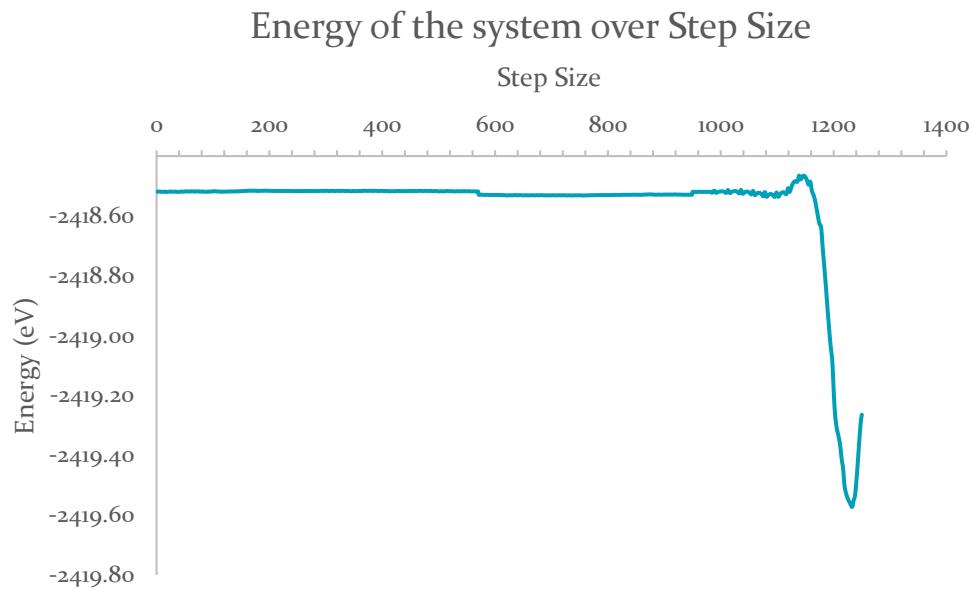


Figure 11: The change in energy of the system over the step size

The system energy remains relatively constant from step 0 to step 1000 hence, the change in energy due to the bonds breaking and forming is not encompassed by the graph, the only significant change occurring is at step 1100 where the energy decreases significantly by -1.06eV. This decrease in energy represents the formation of a more stable structure as it is at a lower energy than the initial structure. It would appear that the change in energy of the system is due to molecular rearrangement rather than bond breaking and forming.

This is also justified by the lack of energy changes of a unitary order of magnitude in figure 11; the expected energy changes should be: +3.9eV for the P-O bond breaking, +4.81 eV for the O-H bond breaking and -4.81 eV for the O-H bond forming, resulting in an overall change in energy due to bonds breaking and forming equal to +3.9eV. Such a large change is not present anywhere in figure 11. The large energy change between steps 1150 and 1234 is better understood when looking at the change in dihedral angle of the two remaining OPOH branches in figure 10:

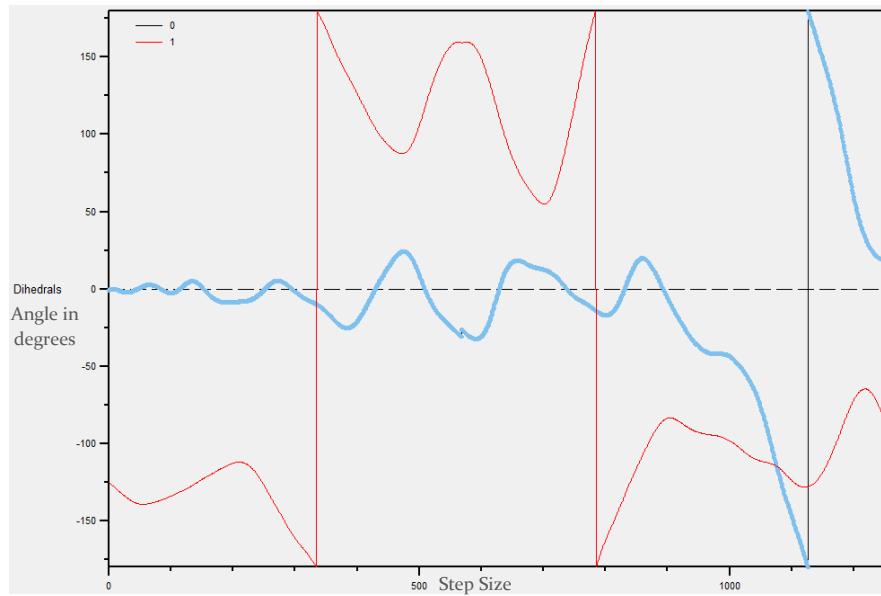


Figure 12: OPOH dihedral angles over step size

By comparing figure 12 with figure 11 it can be seen that the large change in energy corresponds to a 285° change in the OPOH dihedral angle, this is because the molecule finds a new preferred equilibrium orientation. Hence, the -1.06eV energy change is due to molecular reorientation, this observation can also be obtained when looking at the change in temperature of the system over step size in figure 13:

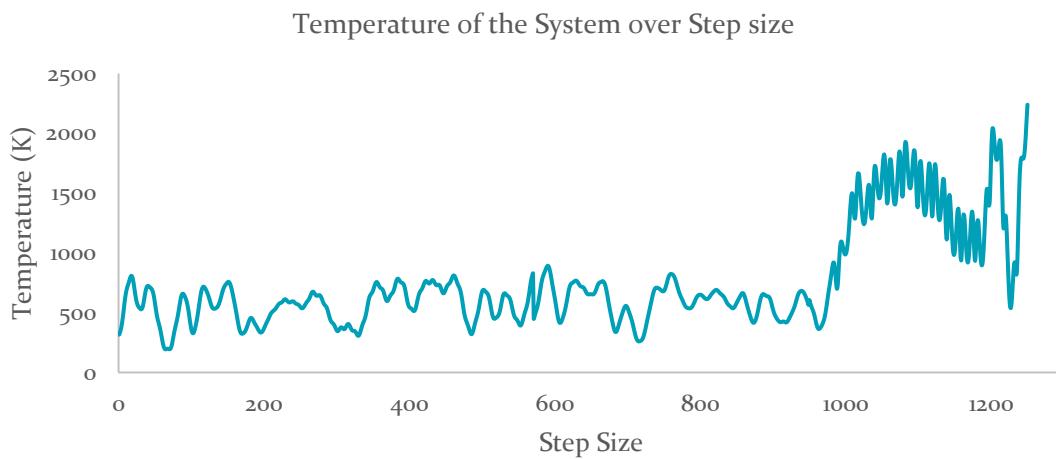


Figure 13: Temperature against Step Size for the monoanionic phosphorane (PO_5H_4^-)

From figure 13 a large temperature change occurs after frame 960, whereas previously the temperature of the system oscillated between 194K and 879K. After frame 960 the temperature increases dramatically over a range of just 95 frames to 1860K. This value then drops to 906K before rising sharply again to 1969K, after which another sharp plunge occurs to 537K followed by another very steep rise in temperature to 2240K. The sharp plunge in temperature to 537K matches with the sudden change in energy in figure 11 and the large change in dihedral angle in figure 12 at frame 1234 which represents the structural change of the molecule.

What can be argued is that there is a range of possible ‘bond breakage’ and ‘bond formation’ lengths; when inputting the cutoff distance what value must be inputted? If the default 1.5 Å is left, then this results in bonds forming and breaking which do not correspond to what is actually occurring in the system. If a smaller value is used closer to the equilibrium value of the O-H bonds (such as 1 Å) then the VMD simulation would give more representative results and probably make events such as bond formation and bond breakage in the VMD simulation match much closer to characteristic peaks and troughs found in the energy and temperature graphs (figures 11 and 13).

CONCLUSION

From the data gathered it was concluded that the CPMD code used allowed for a far better approximation of the structural changes occurring in the diazene and P(OH)₅ structures compared to when using OPLS. However, OPLS does relative justice to the neutral diazene and P(OH)₅ molecules in that the angles and bond lengths are relatively close to those calculated using CPMD. However on the atomic scale, the quantum mechanical nature of atoms must be taken into account, promoting CPMD as the better code to use to get the full picture of what is happening.

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