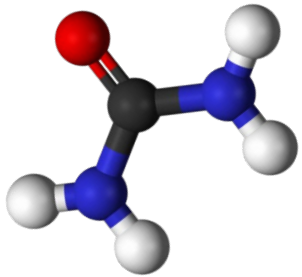
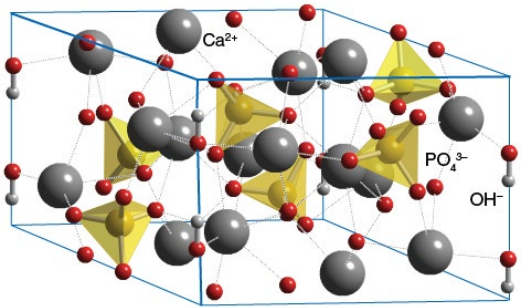
SIMULATION OF UREA - HYDROXYAPATITE BY USING DENSITY FUNCTIONAL THEORY (DFT)





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INTRODUCTION

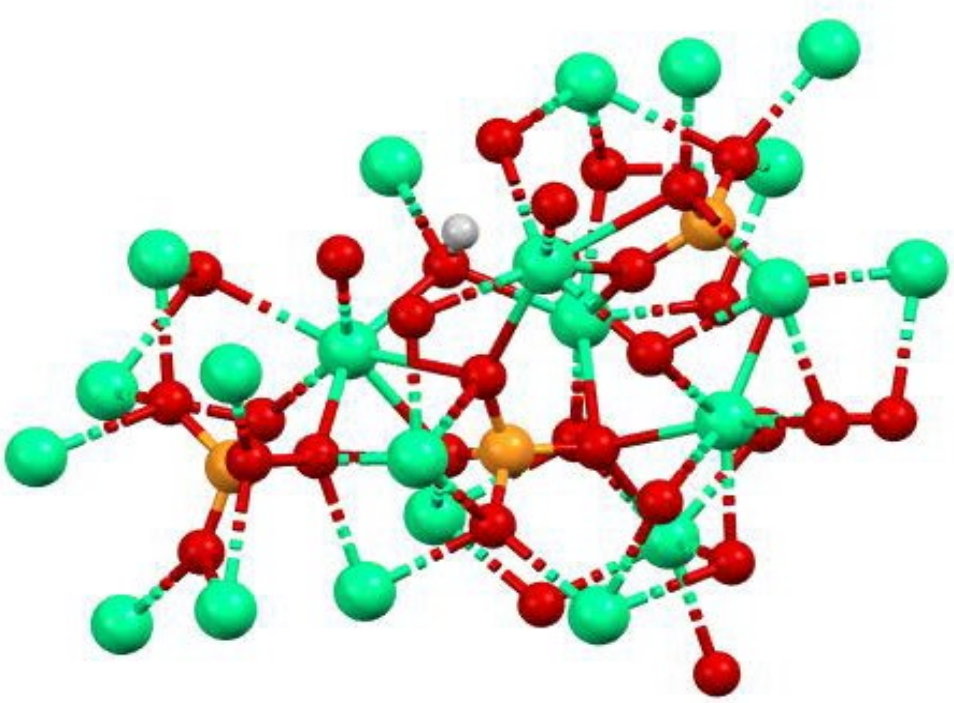
- Nitrogen and phosphorus are the two main important macronutrients for the growth and yields of agricultural crops
- But, due to environmental factors, these nutrients can be easily washed off before reaching the crops.
- These losses of nutrients can give more harm to the ecology, health and economy instead of benefits.
- So, in order to overcome these problems, slow-release fertilizer has been introduced to the agricultural field as it can help in releasing nutrients to the crops in a slow manner.

- The effectiveness of urea and HA as slow-release fertilizer had been proved in previous experimental results.
- For example ; the application of slow-release technology by using urea coated with HA nanohybrids shown that rice crops yield growing well with only 50% concentration of urea used.
- In a complementary manner, this computational study was using DFT and concentrating in depth on interaction between urea and HA in relative stability, structural and electronic properties as it not has been elucidated yet.
- This new findings had been compared with possible comparison with the experimental results from the previous studies and discussed on the next section.

METHODOLOGY

- Gaussian 09 suite of program (Frisch et al., 2013)
    - implementing the scheme of Density Functional Theory (DFT)
    - at level B3LYP/6-31G(d,p). B3LYP is a hybrid functional method that has been widely used these days
- This combination method of DFT and basis set level at 6-31G(d,p) has been used in many previous studies in adding polarization to improve the results
- Multiwfn program was used to identify the topology analysis between urea and HA (Lu & Chen, 2012a, 2012b)

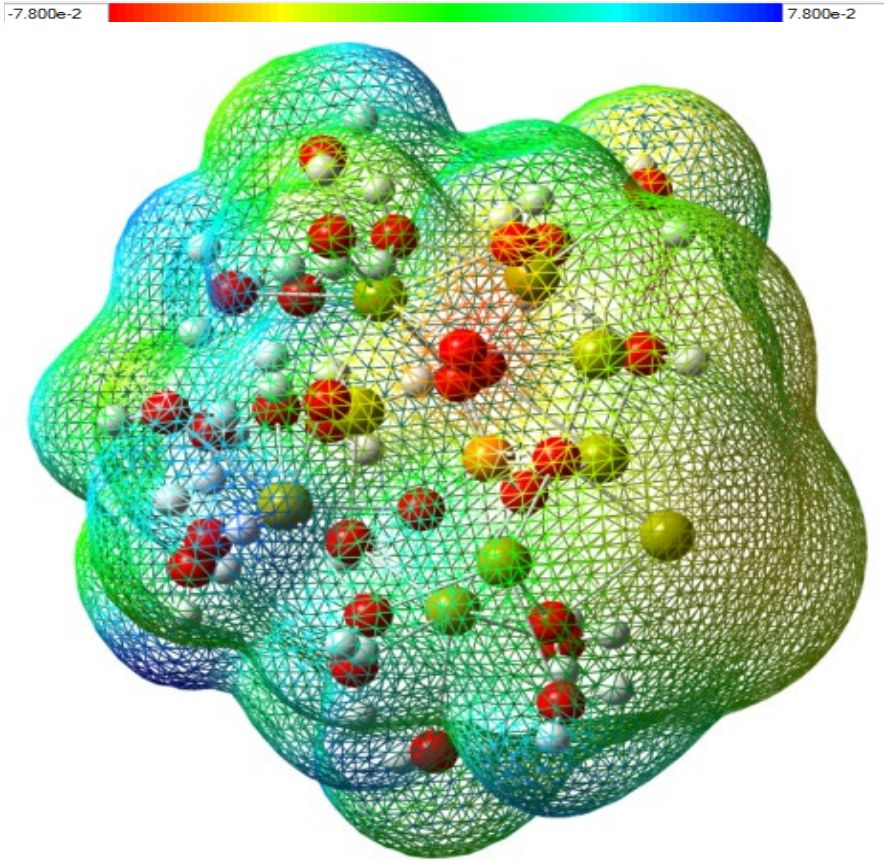
Crystal Structure



Crystal structure of monoclinic HA as shown in Figure 1 was obtained from a report by (Elliott, Mackie, & Young, 1973)

- A cluster model was crafted out of the crystal structure
- The outermost layer consists of oxygen atoms, were terminated on hydrogen-terminated system

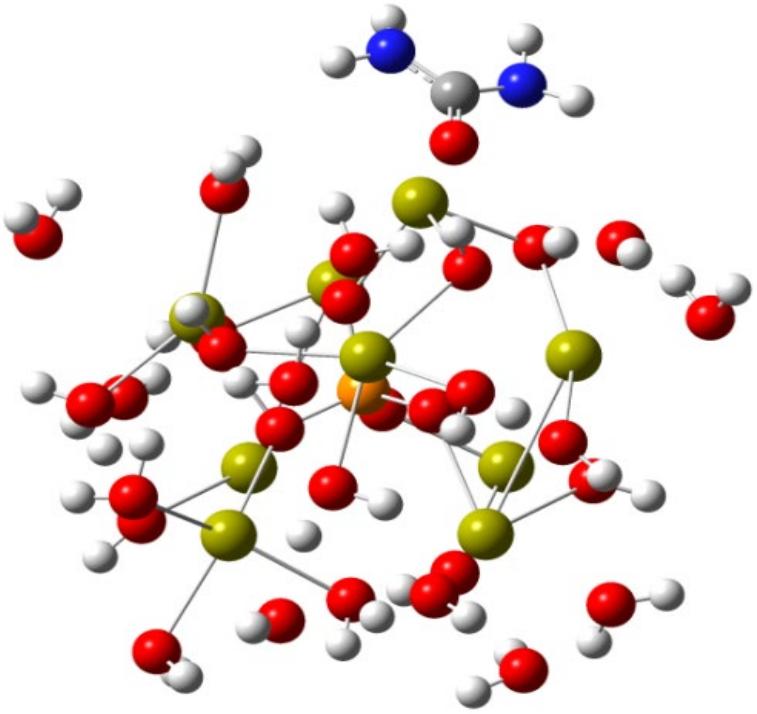
Potential Energy Surface of HA



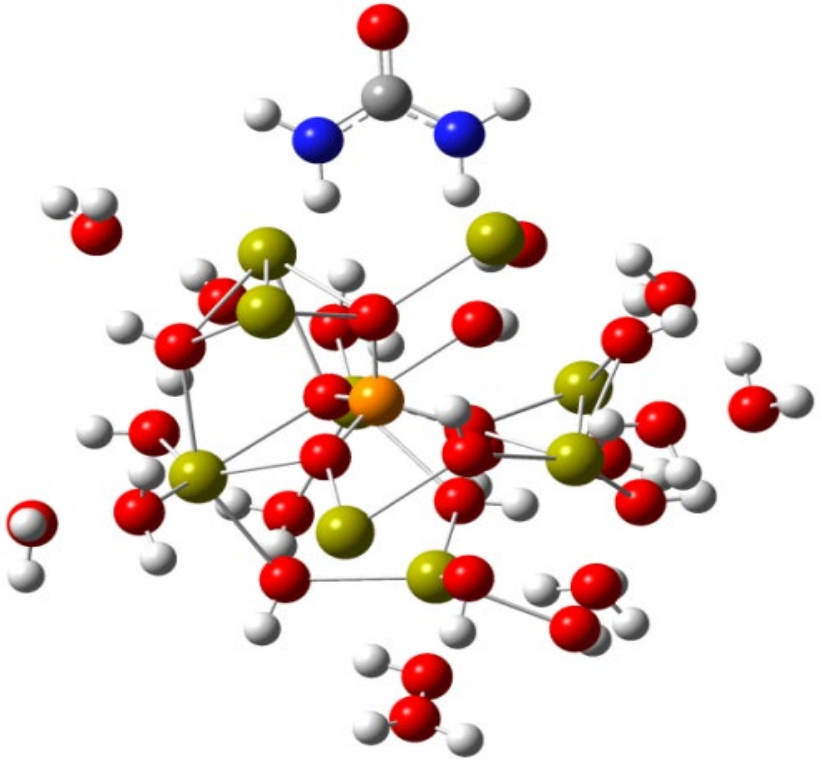
- This PES of HA was mapped to show which region is suitable for placing urea.
- Blue regions – Positive charge (nucleophile activity)
- Red regions – Negative charge (electrophilic activity)

Urea

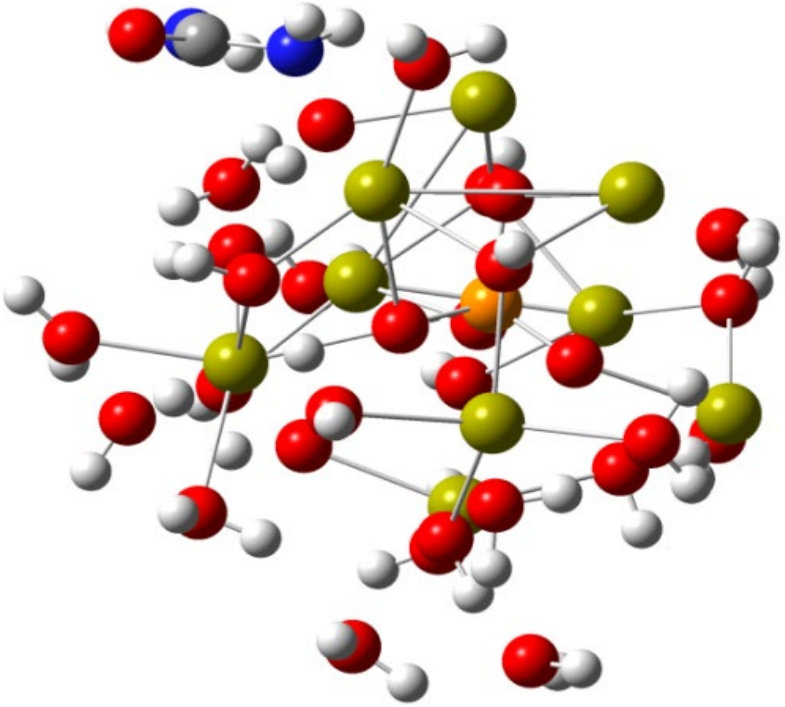
- Urea was initially placed based on chemical intuition of possible interaction of the urea molecule with the surface of HA.
- It was placed on the slight negative charge of HA surface which is on the yellow region.
- Each combination of urea and HA have been placed in different places with different positions. They have been labeled as structures A, B, C and D.
- For structure B and C, they were distinguished by the vertical and horizontal positions of urea at the same placed on HA surface.



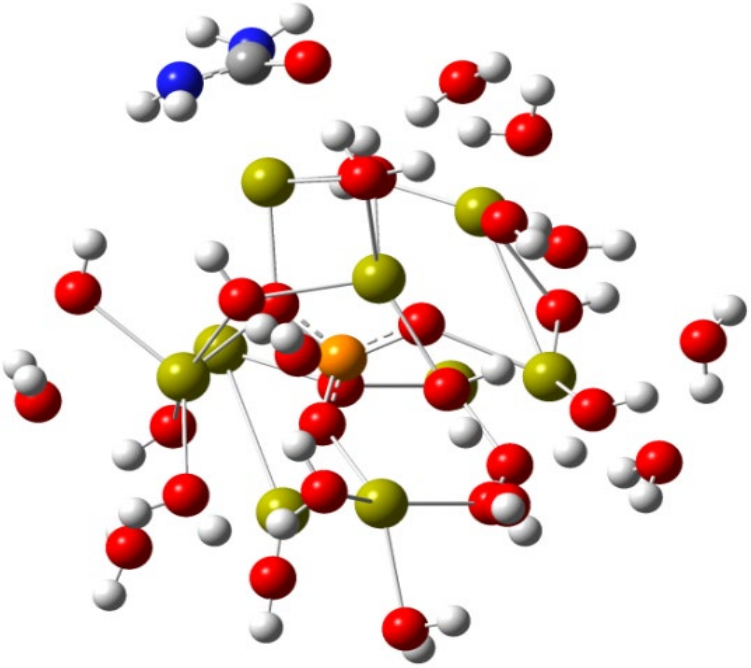
Structure A



Structure B



Structure C



Structure D

$$E_{int} = E_{HA+Urea} - (E_{HA} + E_{Urea})$$

- Where ;
  - E_{int} = Energy interaction between urea and HA
  - $E_{HA+Urea}$ = Energy after minimizing the structure/system
  - E_{HA} = Energy of same structure after removing urea
  - E_{Urea} = Energy of same structure after removing HA

- To determine the relative stability of urea and HA by calculating the strength of interaction between urea and hydroxyapatite
- Using this formula, a more negative value of interaction energy, E_{int} indicates stronger interaction energy between urea and HA

RESULTS AND DISCUSSIONS

Structures	Interaction Energy (eV)
A	−0.9719
B	−1.2245
C	−1.3395
D	−1.1242

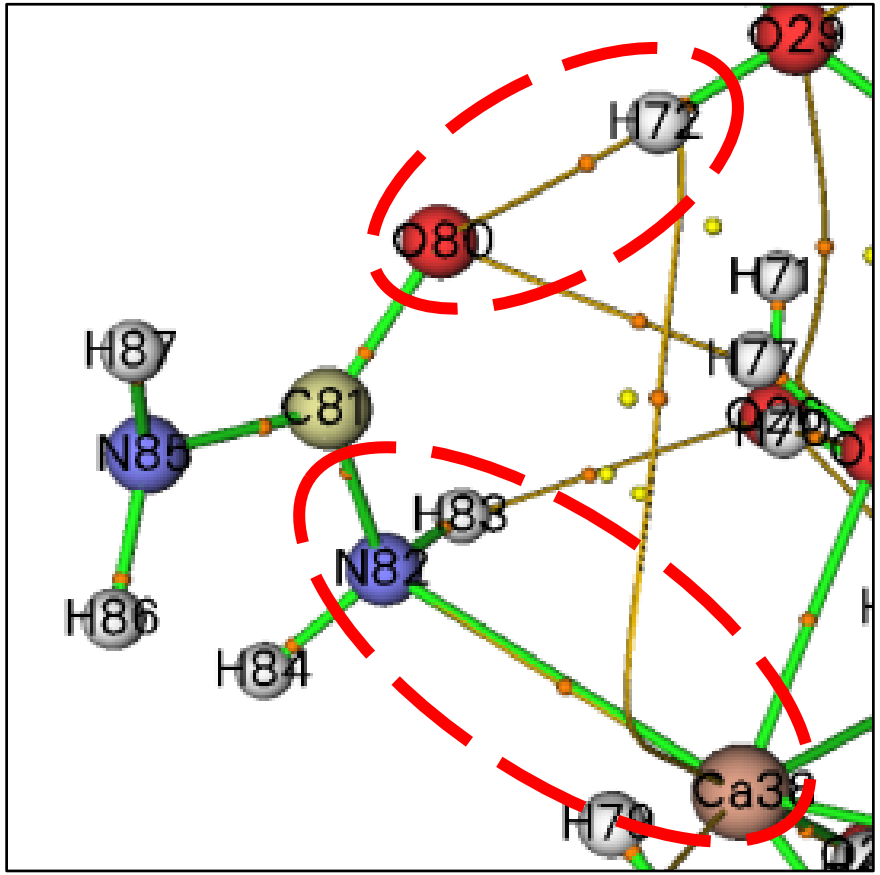
- Structure C has the most stable structure while structure A is the least stable
- The stability of these combinations does not differ significantly, as the energy changes around 0.1 ev between a combination with the next lower combination

Topology Path

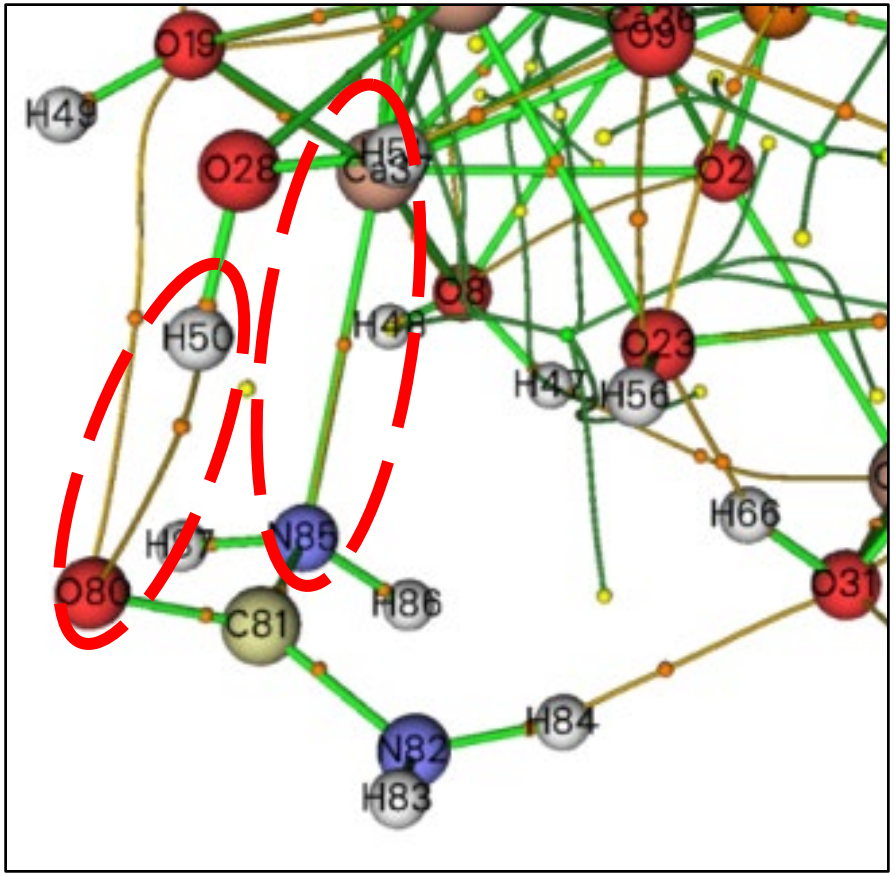
- All structures (A, B, C and D) show a new formed bond between calcium atom in HA and nitrogen atom in urea molecule.
- This is agreed by the previous experimental study, that level energy of N 1s at core level has moved toward higher level energy may due to the new bonding formed between nitrogen atom in urea with HA. (Kottegoda et al., 2017)

- In addition, previous studies have also mentioned that hydrogen bonding were formed between oxygen atom in urea and hydrogen atom in HA. (Kottegoda, Munaweera, Madusanka, & Karunaratne, 2011; Kottegoda et al., 2017)

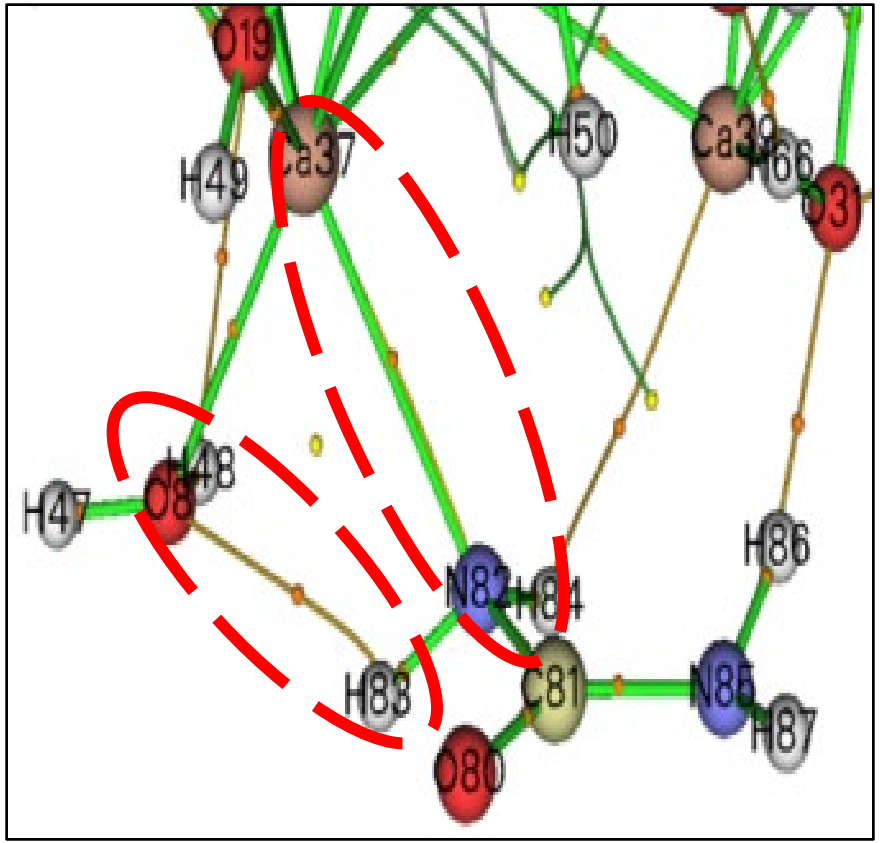
- For all the structures in this study, hydrogen bonding were found between
  - O atom in urea and H atom in HA and/or
  - O atom in HA with the H atom in urea.



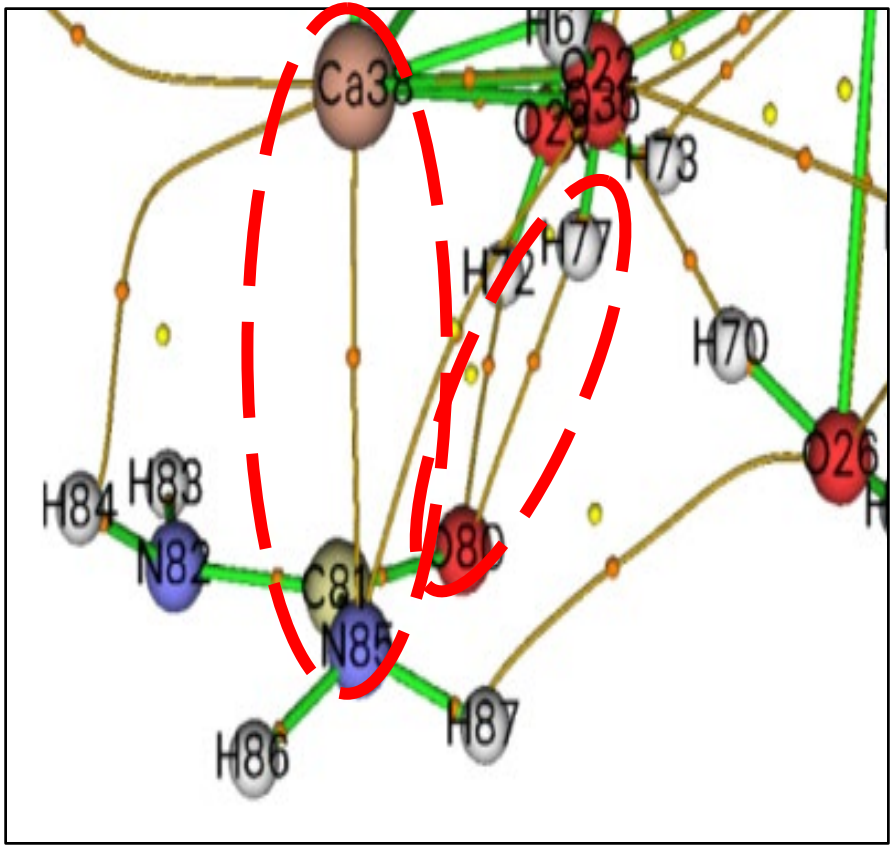
Structure A



Structure B



Structure C



Structure D

Bond Length

Structures & Labels	Bond length (Å)
A (N82-Ca38)	2.8291
B (N85-Ca37)	2.6430
C (N82-Ca37)	2.6663
D (N85-Ca38)	2.8508

- Structure B has the shortest bond length means calcium atom and nitrogen atom has very strong interaction.
- Meanwhile, structure D has the longest bond length means the atoms have least interaction.

CONCLUSION

- As stated by previous studies, new bonds formed between urea and HA.
- In this project, by using Density Functional Theory (DFT) and topology analysis, has proved and shown that new bonds can formed between urea and HA.
- Compare to all structures, structure C has the most stable as it has the lowest interaction energy while for bond length structure B has the shorter bond length.