

Stability and Electronic Properties of Urea in Different Arrangements: A DFT-Based Study

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ABSTRACT

In this report, the results of the investigations on the stability and the electronic properties of urea in different arrangements are presented. Three types of arrangements of the urea molecules are modelled, namely chain cluster (CC), ribbon cluster (RC), and spherical cluster (SC). In each of these clusters, the sizes of the clusters are increased systematically, hence creating opportunity to understand better the intermolecular interaction of urea crystal. The electronic properties in terms of molecular orbital and electrostatic potential are also studied in this work. Using model chemistry BP86/DEF2-TZVP as implemented in Gaussian 09, together with a few energy-improving schemes, it was found that the CC has the most stable molecule arrangement, in agreement with the previous studies. RC and SC, on the other hand, have weaker intermolecular interactions. The MO and ESP studies show that the existence of the reactive sites may be connected to the relative stability between these three clusters.

Keywords: *electronic properties; urea; ribbon cluster; spherical cluster; chain cluster.*

1. Introduction

The urea molecules have been one of the most thoroughly investigated systems either experimentally or theoretically. This is due to wide usage of urea in multiple industries. Previously, urea had been shown to have high nonlinear optical properties (Luo, Yang et al., 2011; Masunov, Tannu et al., 2017). Urea is also an important moiety in the pharmaceutical industries as it is used in a broad range of drugs (Díaz, Palop et al., 2017). However, the understanding and designing of the intermolecular interaction that dictates crystal packing of urea is still unclear. The studies had shown that urea molecules provide a wide range of possible hydrogen-bonds due to having the C=O and N-H groups in clusters (Keuleers, Desseyn et al., 1999). Specific interaction such as hydrogen bonding can significantly influence the electronic structure of the complexes. The previous study also shows that the main contribution to the intermolecular interaction energy is due to the long-range electrostatic and the short-range exchange repulsion (Dovesi, Causa' et al., 1990). They also suggest that the influence of a dispersion interaction on the hydrogen bond formation in the urea crystal should be negligible. However, another study had stated that the intermolecular correlation effects contribute significantly to the stabilization energy of the urea molecule in the crystal when compared to the gas phase (Ayala & Scuseria, 2000).

In this work, we reported the systematic studies of the interaction in urea crystal with state-of-art techniques, with the objective to provide a better understanding of the nature of binding forces in the molecular urea systems.

2. Method

In a theoretical study, reliable computational prediction of lattice energy is of crucial importance to simulate the structure of organic compound (Feng & Li, 2006). Reliable computational prediction enables the accurate treatment of different types of intermolecular interactions, including electrostatics, induction and dispersion. Kohn-Sham density functional theory (KS-DFT) is a method known to account for electrostatic and induction interactions of molecular crystals (Kohn, Becke et al., 1996; Sousa, Fernandes et al., 2007). However, semilocal functionals fail to adequately model the dispersion interaction (Pérez-Jordá & Becke, 1995). Thus, development of dispersion-including DFT model had gained attention from researchers. Semiclassical dispersion correction is known to be less computationally demanding than other dispersion correction methods (Beran, 2016). This add-on correction, for example the D3 scheme formulated by Grimme et al. (Grimme, Antony et al., 2010) is enough in predicting the organic compound behaviour (Moellmann & Grimme, 2010). Further refinement of this method includes the damping scheme. Similar to D3, this new method, known as D3BJ (Grimme, Ehrlich et al., 2011) does not affect the long range decay

of the dispersion energy but improves the dispersion energy decays to zero at short range part of D3. D3BJ has proven its reliability as it gives less average error compared to non-dispersion corrected calculation and D3 dispersion-corrected DFT scheme (Grimme, Huenerbein et al., 2011; Christensen, Kubař et al., 2016). Hence, D3BJ is preferred over D3 scheme.

Crystalline solid is structured from an infinite number of molecules which include the intermolecular interaction effects from the neighbouring molecule. Thus, to elucidate this environment, the interactions between neighbouring molecules must be considered. However, supramolecular approach usually has the basis set superposition error (BSSE) due to unbalanced basis set expansion of monomer. The counterpoise (CP) scheme by Boys and Bernardi can be used for this problem (Boys & Bernardi, 1970) but it only considers intermolecular BSSE of non-covalently bound dimer complexes. Another scheme, known as geometrical counterpoise (gCP), offers estimation of the inter- and intra-molecular BSSE for DFT calculations with various basis sets (Kruse & Grimme, 2012). gCP estimates the correction based only on the cartesian coordinates of the molecules or complexes.

Three different aggregates pattern was studied in this work to cover different possible adjacent interactions. The three different aggregates pattern are chain cluster (CC) (Figure 1a), ribbon cluster (RC) (Figure 1b) and sphere cluster (SC) (Figure 2).

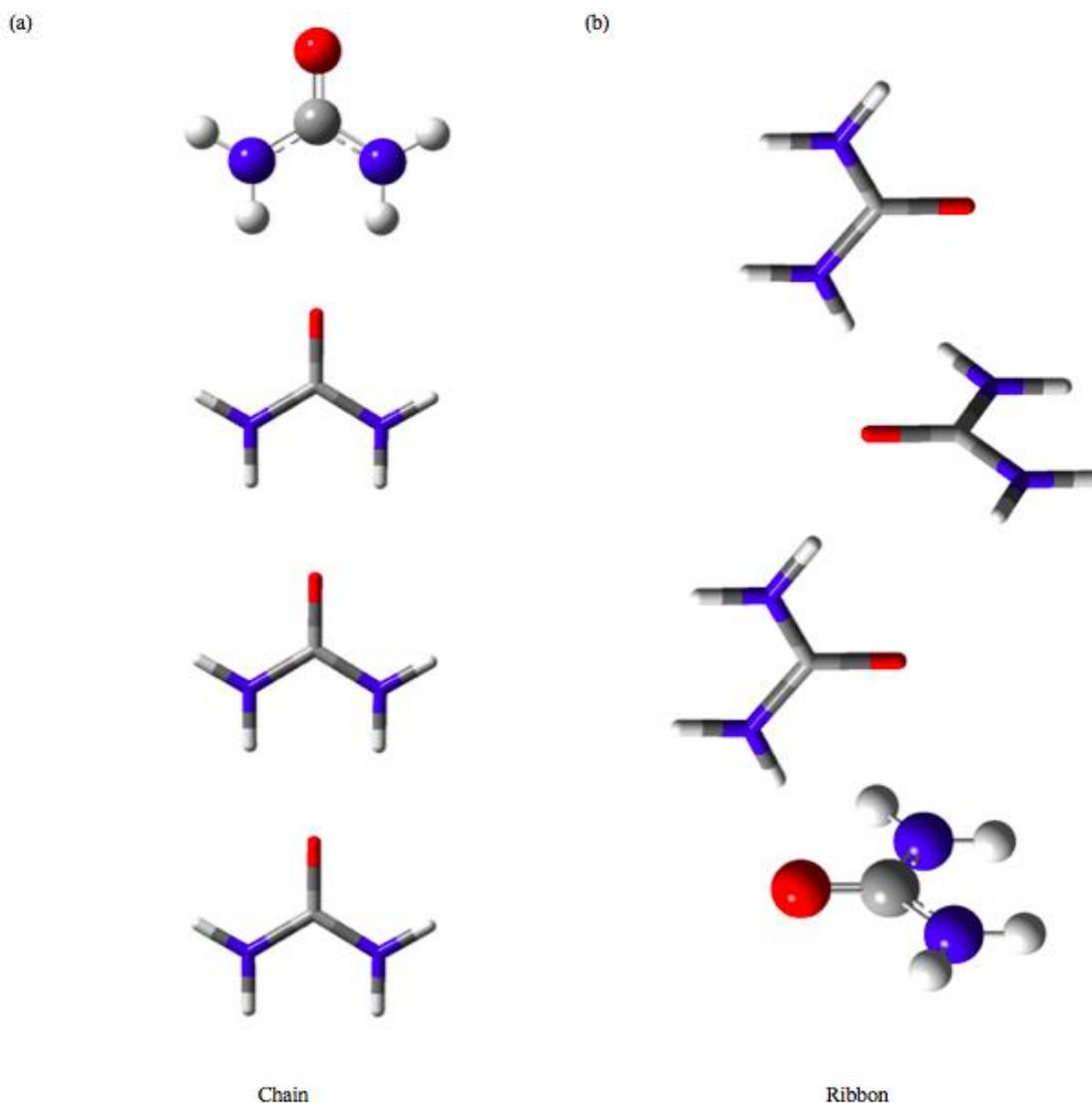


Figure 1. (a) CC and (b) RC pattern for 4-molecule urea.

CC and RC are systematically extended with increasing number of molecules from the main urea (ball and stick). However, for SC, the increasing number of molecules depends on the distance from the main urea (ball and stick urea). Thus, the distance was starting from 3, 4, 5, and 6 Angstrom for 4, 8, 15 and 23 molecules.

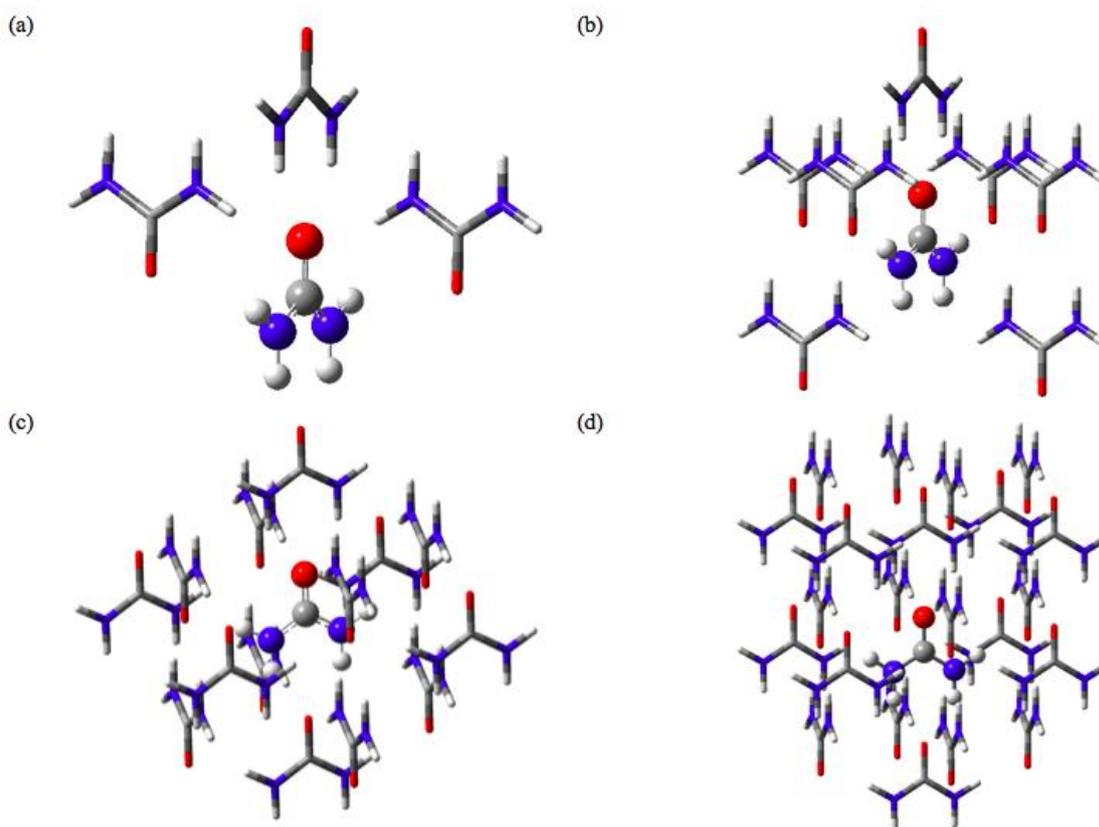


Figure 2. SC pattern of (a) 3 Angstrom, (b) 4 Angstrom, (c) 5 Angstrom, and (d) 6 Angstrom distance from main urea.

To find the stability of the urea cluster, the relative energy per molecule is calculated with the formulae of

$$E_{\text{rel}} = \frac{E_{\text{tot}}}{n} - E_{n-1} \quad (1)$$

where n is number of molecules while the E_{tot} is the total energy which described as

$$E_{\text{tot}} = E_{\text{DFT}} + E_{\text{d3bj}} + E_{\text{gcp}} \quad (2)$$

E_{DFT} is the DFT energy, E_{d3bj} is dispersion correction energy and E_{gcp} is the counterpoise correction energy.

3. Results and Discussion

3.1. Relative Energy per Molecule

The results for the stability of the urea cluster using systematic cluster calculations are tabulated in Table 1 and displayed graphically in Figure 3. The inclusion of the gCP and D3-BJ corrections (not shown in the tables and figure) rendered the E_{total}/n more negative than those without. As the D3BJ are negative values, while gCP are smaller positive values, the net result is the increased cohesiveness of the molecules. Hence, the inclusion of the correction schemes gave a more strongly bounded picture for the molecules.

Using Equation 1, the E_{rel} for all types of cluster become more negative as the number of molecules is increased, indicating the increase stability of the urea in the larger cluster. This in line with the notion that as the cluster becomes larger, there are more interactions between the molecules. We anticipate that, with the inclusion of more molecules in a cluster, E_{total}/n will eventually reach a stable limit. The decreasing pattern for all types of clusters can be attributed to the increasing intermolecular interaction between cluster molecules as the number of molecules is increased.

Comparing all three patterns of the urea clusters, **CC** is always more negative than in **RC** and **SC**. This shows that **CC** is always more stable than **RC** and **SC**. This result agrees with the previous study that compared the difference between the **CC** and **RC** (Masunov & Dannenberg, 2000; Gora, Bartkowiak *et al.*, 2002). Both these cluster patterns have the same trend in increasing stability (more negative) where the

gradient of the curve is decreasing compared to the initial increase from the dimer urea. From Figure 2, sphere cluster has a centre molecule (ball and stick form) that have interactions with neighbouring molecules surrounding it while outer molecule (stick form) only has an interaction of inner molecules. Thus, the E_{rel} of the **SC** is not converging as fast as the **CC** and **RC** as the outer molecules have more contribution to the stability of the cluster. However, it is assumed at the larger number of molecules, system starts to possess the solid state environment for the centre molecule where the outer molecules have less effect on the overall interaction. The E_{rel} of **SC** is due to the molecules in this type of cluster have mixed arrangements between chain and ribbon.

Table 1. Results of relative energy (eV) for CC, RC and SC.

No. of Molecules	Relative Energy (eV)		
	CC	RC	SC
1	0.0000	0.0000	0.0000
2	-0.2228	-0.1294	-0.1806
3	-0.3392	-0.1590	
4	-0.4074	-0.1718	-0.1874
5	-0.4516	-0.1827	
6	-0.4824	-0.1867	
7	-0.5050	-0.1925	
8	-0.5223	-0.1942	-0.2102
9	-0.5359	-0.1979	
10	-0.5470	-0.1987	
11	-0.5560	-0.2013	
12	-0.5637	-0.2017	
13	-0.5701	-0.2037	
14	-0.5757	-0.2038	
15	-0.5806	-0.2054	-0.3583
16	-0.5848	-0.2054	
17	-0.5886	-0.2068	
18	-0.5920	-0.2067	
19	-0.5950	-0.2078	
20	-0.5977	-0.2077	
21			
22			
23			-0.4735

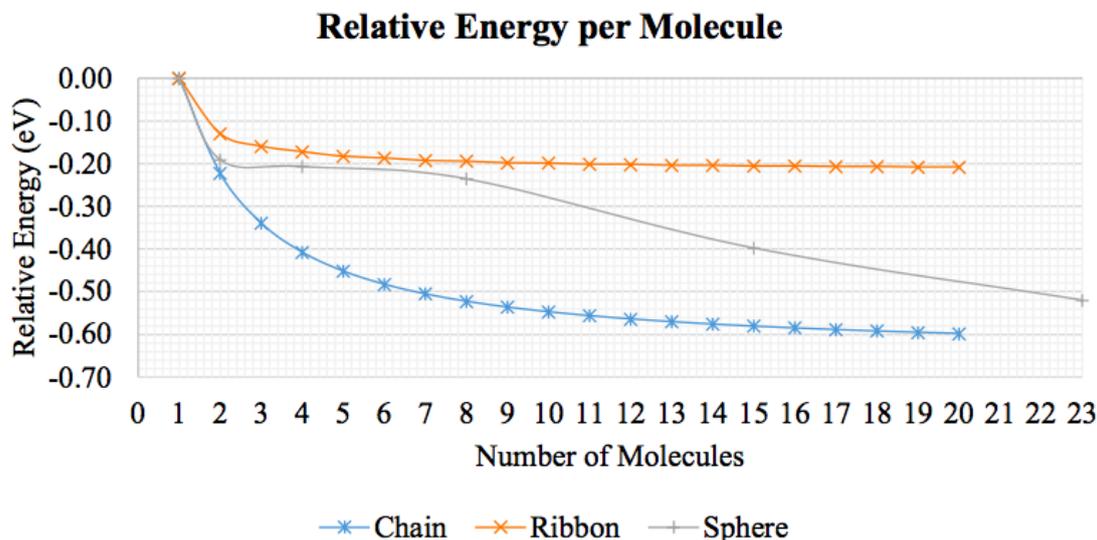


Figure 3. Relative energy per molecule for CC, RC and SC.

3.2. Dipole Moment

The behaviour of the dipole moments of the **CC** and **RC** are similar to the previous studies (Masunov & Dannenberg, 2000). As shown in Table 2, the dipole moment/molecules (DM_m) for **CC** increases as the size of the cluster increases. The increment becomes smaller and the curve is flat at dipole of 7 Debye as shown in Figure 4. For the **RC**, the DM_m fluctuates, as can be seen in Table 3 and the curve in Figure 4. The cluster with even number of molecules has an almost zero DM_m because the arrangement of the **RC** is centrosymmetric. As **SC** contained mixed arrangements of chain and ribbon, its DM_m also fluctuates.

Table 2. The dipole moment of the CC, RC and SC pattern.

No. of Molecules	Dipole Moment/Molecule, DM_m		
	CC	RC	SC
1	4.7088	4.7088	4.7088
2	5.6554	0.4564	5.6554
3	6.1122	1.2156	
4	6.3749	0.4058	0.5679
5	6.5439	0.5463	
6	6.6611	0.4082	
7	6.7470	0.2614	
8	6.8126	0.4139	2.5031
9	6.8643	0.1035	
10	6.9060	0.4186	
11	6.9404	0.0032	
12	6.9693	0.4224	
13	6.9938	0.0662	
14	7.0149	0.4254	
15	7.0333	0.1171	0.4307
16	7.0494	0.4277	
17	7.0637	0.1560	
18	7.0764	0.4296	
19	7.0878	0.1867	
20	7.0981	0.4312	
21			
22			
23			0.3642

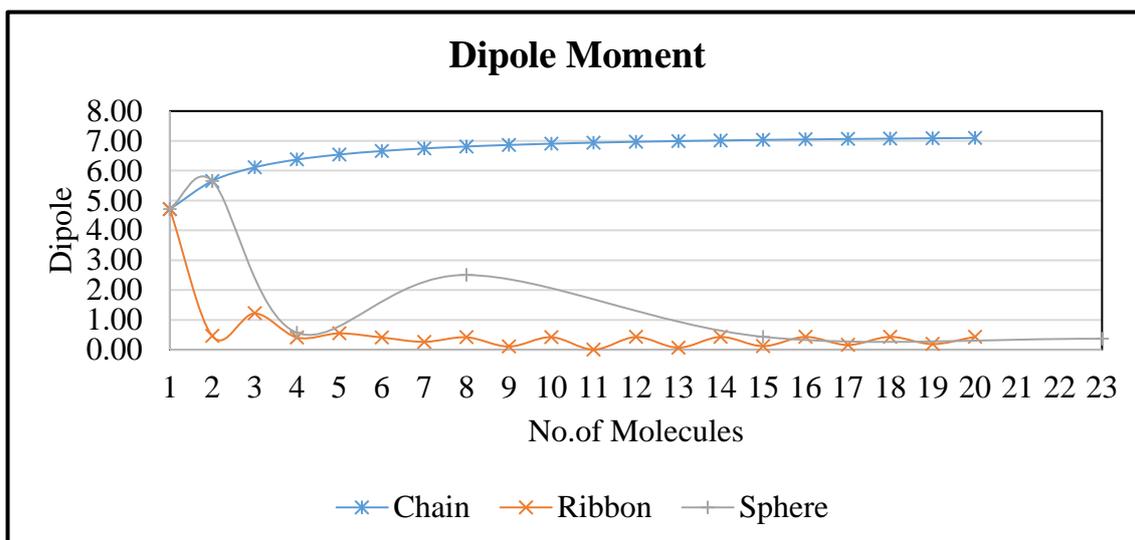


Figure 4. The dipole moment of the CC, RC and SC pattern.

3.3. Molecular Orbital

To have a better understanding of the interaction between the urea molecules in different arrangements, the molecular orbital (MO) and electrostatic potential (ESP) analysis had been discussed. The MO represents the region where electron occupying that orbital is likely to be found in a molecule. The highest occupied molecular orbital (HOMO) of the molecules shows the nucleophile sites which are rich in electrons. The lowest unoccupied molecular orbital (LUMO) of the molecules are the electrophile sites which are poor of electron. This is the region that likely to accept an electron.

MO for 1-molecule urea is shown in Figure 5. As in Figure 5 (a), HOMO, the contributions from orbitals of oxygen, nitrogen and hydrogen. This shows that this site would donate their electron as the interaction occurs between molecules. LUMO in Figure 5 (b) shows that electron is likely to interact with the hydrogen site of the urea. This is due to the hydrogen in the electron deficient site of the molecule.

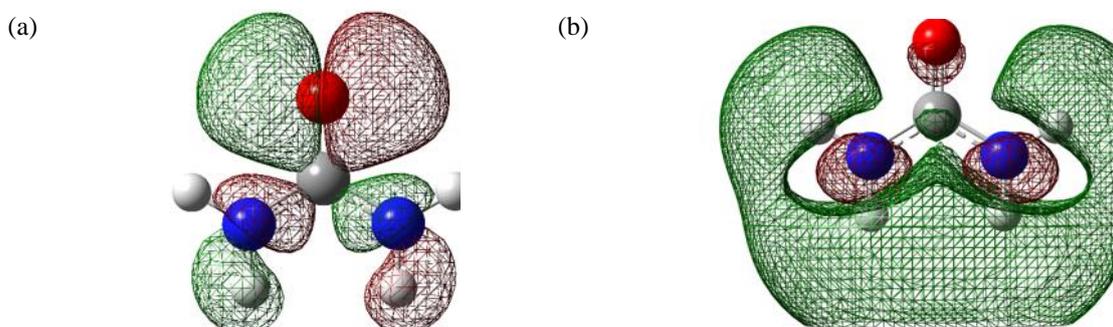


Figure 5. The molecular orbital of (a) HOMO and (b) LUMO for 1 molecule urea

Figure 6 shows the (a) HOMO and (b) LUMO for CC of urea. As the number of molecules increase from dimers to 4-molecule urea, HOMO region (Figure 6 (a) of CC shows that MOs only occupied at one side of the clusters. Hence only one side of CC is prone to donate an electron. LUMO for the chain cluster is consistently visual at the opposite end of the chain cluster compared to the HOMO. These show that the opposite of HOMO site of CC is prone to accept an electron from another molecule. Having said this, the centre region of the CC is not an active region for reactivity.

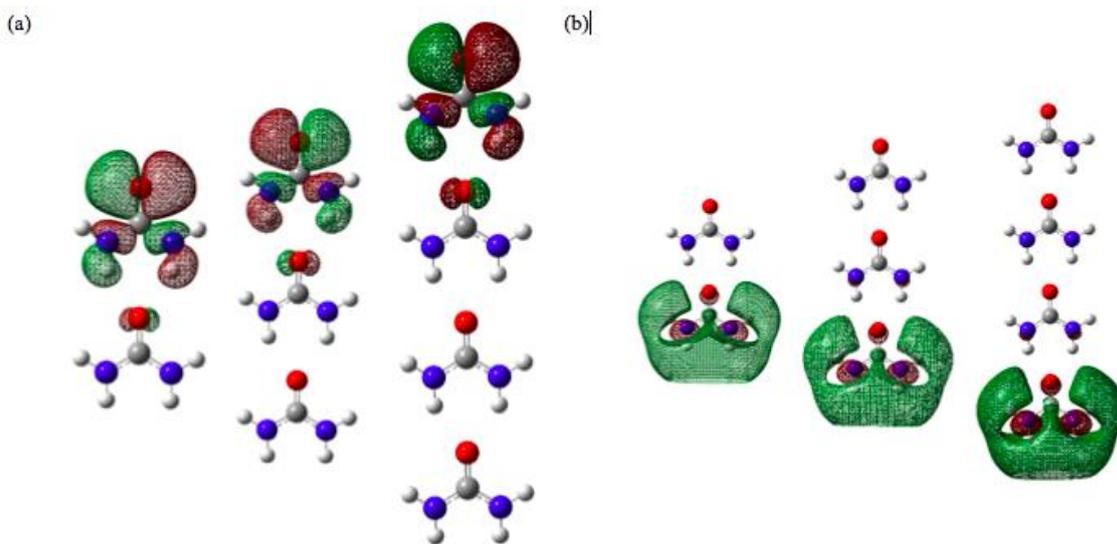


Figure 6. The molecular orbital of (a) HOMO and (b) LUMO for 2, 3 and 4-molecule CC

In Figure 7 (a), HOMO for **RC** appears at the middle molecule of the cluster with even number of molecules and at outer molecule for the cluster with odd number of molecules. As the number of molecules increase, the HOMO repetitively exists in the middle and outer molecule of the **RC**. It indicates that the site of the electron donor is repetitively changing as the number of molecules increase. For LUMO region (Figure 7 (b)) for the **RC** also shows a similar pattern where the LUMO is visual at the outer molecule for cluster with even number of molecules and at inner molecule as the number of molecules in the clusters is odd. This repetitive change of the donor and acceptor shows the interaction of the ribbon cluster is changing as the number of the molecules in cluster is changing. Thus, this would agree with the dipole moment result that there is fluctuation to the dipole moment of the cluster.

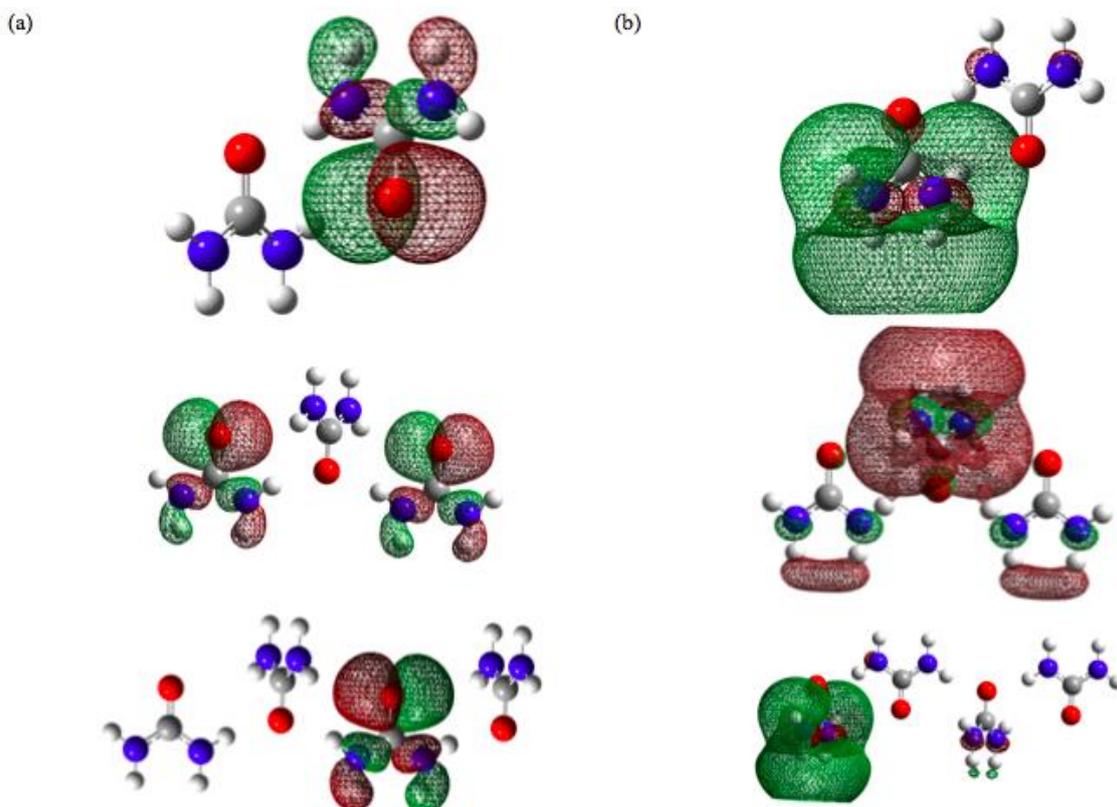


Figure 7. The molecular orbital of (a) HOMO and (b) LUMO for RC

Figure 8 shows the HOMO and LUMO of the **SC** of the dimer, 4-molecule and 8-molecule clusters. The HOMO and LUMO exist randomly as the number of molecules increase. This is to be expected as a result of mixed arrangement of the molecules in **SC**.

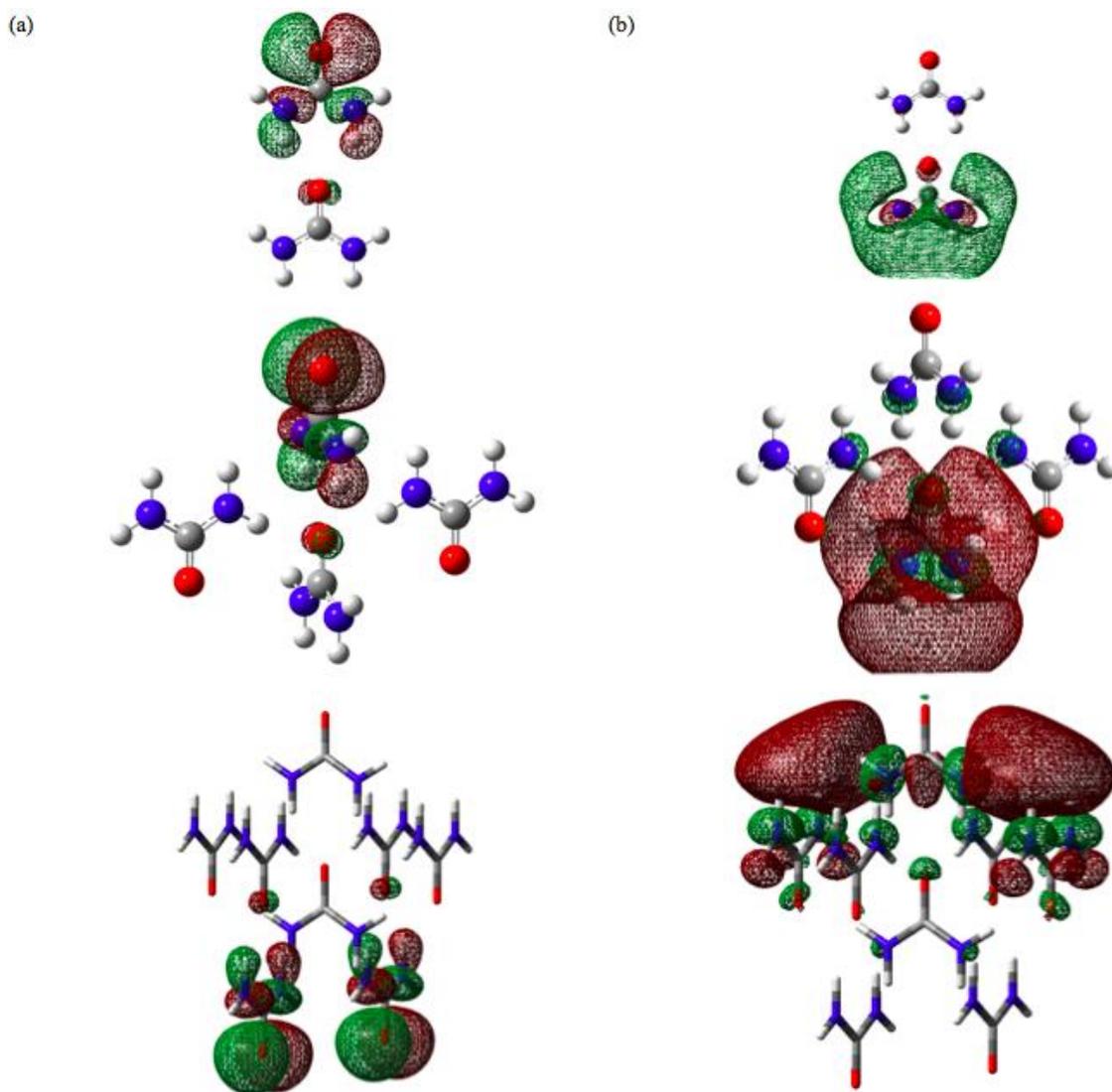


Figure 8. The molecular orbital of (a) HOMO and (b) LUMO for SC

3.1.4. Electrostatic Potential (ESP)

Electrostatic potential (ESP) analysis is shown in a range of colours. Colours change from blue-green-red according to the average ESP of the compound. Blue colour indicates low ESP which shows the nucleophilic site of the molecule while red colour indicates high ESP where the electrophilic site of the compound. Green is the site with low reactivity as the potential are stable from overall potential of the molecules.

1-molecule urea shows the basic interaction site of urea. From Figure 9, ESP shows that the electrophilic interaction would occur at the oxygen atom of the urea molecule. This is due to the oxygen atom is a highly electronegative atom. The blue site of the urea is shown at the hydrogen site of the urea. This shows that this site would attract another molecule.

The region of the ESP changes as the number of molecule increase. The red region of the ESP in urea CC (Figure 10) is similar to 1-molecule urea. However, the red site only appears at the end of the urea CC. Thus, only this site would reactive to donate its electron for the interaction between molecules. The blue region is at another end of the CC. This shows the reactivity of the molecules to attract other molecules occur only at these two regions of the compound. The green colour is visible between the ends of the CC. This green region is broader as the number of molecules increase. This shows that the middle molecules of the urea compound in CC are stable as the number of molecules increase. This result is in agreement with the point of view of MO.

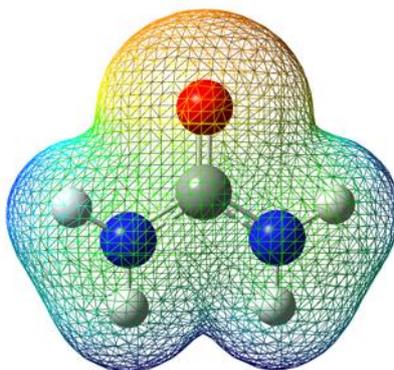


Figure 9. The ESP for 1-molecule urea.

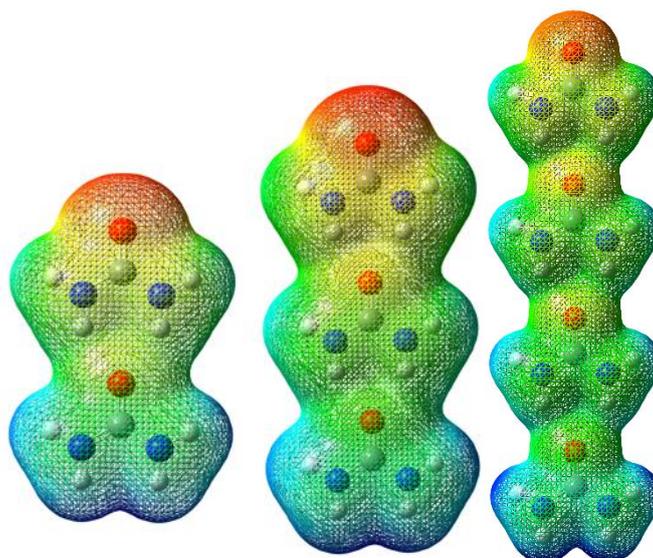


Figure 10. The ESP of 2-, 3- and 4-molecule for CC urea

For the **RC** (Figure 11), as the number of molecules is increased, the distribution of the colour repetitively appears across the cluster. Each molecule is able to react individually, as each molecule has electrophilic (blue site) at each hydrogen atoms and nucleophilic (red site) at the oxygen atom. This would result in the less stable cluster than **CC** as shown in Figure 3.

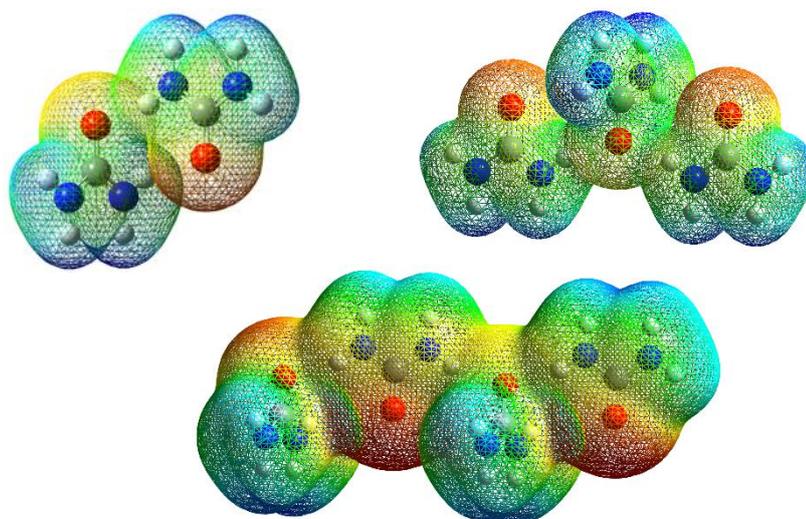


Figure 11. The ESP of 2-, 3- and 4-molecule for RC urea

Figure 12 shows **SC** also shows the same randomness of the ESP surface as in **RC**. The colour range changes to dark blue – light blue – green – yellow – red for dimer and 4-molecules cluster. However, the middle molecule of the sphere cluster changes into green (stable region) colour as number of molecules increase. The outer molecule would have reactive site for the electrophilic and nucleophilic interaction between molecules.

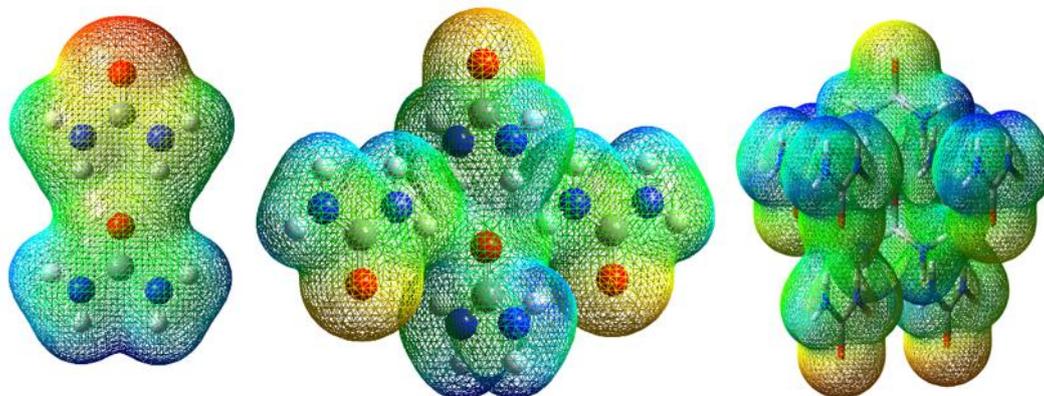


Figure 12. The ESP of 4- and 8-molecule for SC urea.

Comparing the ESP of three types of arrangements (**CC**, **RC**, **SC**), there might be a connection between the size of the green region to the stability of different arrangements. For **CC** which is the most stable cluster, the green region is the largest. For **SC**, with lesser site of the green region, the stability is lower than **CC** but higher than **RC**, which has no visible green region in the cluster.

4. Conclusion

This work studies the nature of the stability and the interaction of the urea cluster in different patterns of chain, ribbon and sphere. The differences in the stability and interaction of the different patterns are primarily due to the hydrogen bond between molecules. The result shows that the chain always has high stability with strong hydrogen bonding between molecules. The chain cluster which has two hydrogen atoms interacting with each oxygen atom is more stable than other cluster patterns. Investigations on the electronic properties revealed that there may be connections between the existence of the reactive sites with the relative stability between these three clusters.

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