

ANALYSIS OF CHITOSAN/POLYVINYLPYRROLIDONE (STRUCTURE, FTIR, ELECTROSTATIC POTENTIAL, HOMO/LUMO ORBITALS) USING COMPUTATIONAL CHEMISTRY

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Abstract— Chitosan and PVP oligomers were analyzed by means of the HyperChem software 8.0v to determine the theoretical structure. Quantum chemical calculation of geometrical structure and energies were studied using PM3 and AM1 methods in where the Gibbs free energy was calculated with a value of -9028 and -5796 Kcal/mol, respectively; these values showed that the reaction was carried out. Quantum chemical calculations are applied to study the (CT) complexes in order to obtain information on structures and other molecular properties like specific interaction of donor and acceptor. The interaction energy contribution comes from the effects of donor-acceptor interactions and π - π interactions. The HOMO and LUMO were simulated by determinate the transition state and energy band gap. Vibrational analysis shows that the band in 3185 cm⁻¹ and shifting of band to lower wave number clearly indicates strong intermolecular interactions between chitosan and PVP. When the PVP oligomers is blended with chitosan, this absorption signal, which is assigned to the stretching vibration of a C=O group in the pyrrolidone ring, tends to shift to a position of somewhat lower frequency.

Keywords— PM3, AM1, Chitosan, PVP, oligomers.

I. INTRODUCTION

Biopolymers have generated significant interest in the areas of biomedical and pharmaceutical sciences (Anupama and Wanchoo, 2012). Chitosan is a natural biopolymer modified from chitin, which is the main structural component of squid pens, cell walls of some fungi and shrimp and crab shells. Chitin and chitosan are copolymers found together in nature. They are inherent to have specific properties of being environmentally friendly and are easily degradable (Boonlertnirun *et al.*, 2008; Zeng *et al.*, 2012; Bautista *et al.*, 2006). The positive charge of chitosan confers to this polymer numerous and unique physiological and biological properties with great potential in a wide range of industries such as cosmetology (lotions, hair additives, facial and body creams), food (coating, preservative, antioxidant, antimicrobial), biotechnology (chelator, emulsifier, flocculent), pharmacology and medicine (fibers, fabrics, drugs, membranes, artificial organs) and agriculture (soil modifier, films, fungicide, elicitor) (Bautista *et*

al., 2006; Kim *et al.*, 2008). The structure of chitosan is very similar to that of cellulose; it consists of β (1-4)-linked D-glucosamine residue with the 2-hydroxyl group being substituted by an amino or acetylated amino group (Fig. 1).

The primary amine groups endow chitosan with many special properties, making it applicable in many areas and readily available for chemical reactions, for example, salt formation with acids. Chitosan is positively charged, making it able to adhere to the negatively charged surface. Chitosan is soluble in diverse acids and able to interact with polyanions to form complexes and gels. It holds antibacterial and antifungal properties. It is safe and nontoxic (Agnihotri *et al.*, 2004; Kim and Rajapakse, 2005; Kumar *et al.*, 2011; Depan *et al.*, 2011; Sionkowska *et al.*, 2011). The polyvinylpyrrolidone (PVP) (Fig. 2) has good film-forming and adhesive behavior on many solid substrates and it is formed films exhibit good optical quality (high transmission in visible range), and mechanical strength (easy processing) required for applications (Rui *et al.*, 2003; Ramya *et al.*, 2008; Zhang *et al.*, 2008).

The amorphous structure of PVP also provides a low scattering loss, which makes it as an ideal polymer for composite materials for different applications. PVP is easily soluble in water, so it is preferred to avoid phase

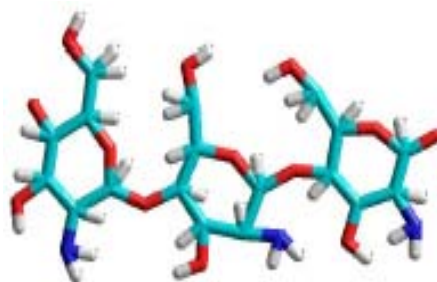


Fig. 1. Chitosan structure (Red: oxygen, white: hydrogen, Blue: carbon and Purple: nitrogen atoms)

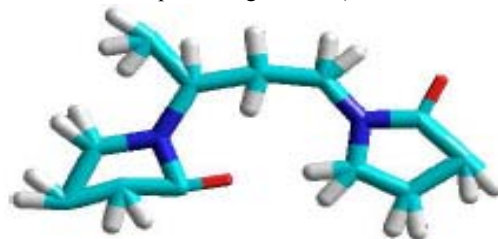


Fig. 2. PVP structure (Red: oxygen, white: hydrogen, Blue: carbon and Purple: nitrogen atoms).

Table 1. FTIR results of chitosan oligomer

Assignment	PM3 (frs. cm^{-1})	AM1 (frs. cm^{-1})
CH (CH_2 -OH) stretching	4491	4374
OH and CH (CH_2 -OH)	3615	367
CH (CH_2 -OH) stretching	3526	3512
OH (CH_2 -OH)	3305	3300
C-N	2053	2041
C-C	1927	1909
C-O (Chitosan ring)	1490	1489

Table 2. FTIR results of PVP oligomer

Assignment	PM3 (frs. cm^{-1})	AM1 (frs. cm^{-1})
CH (PVP ring)	3285	3284
C-C stretching	2261	2248
C=O (PVP)	2133	2113
CH (PVP ring)	3259	3207
C-O, C-C and C-N	1426	1431
NH_2 , CH	1266	1215

separation in the reactions (Sivaiah and Buddhudu, 2011; Sivaiah *et al.*, 2010). PVP is used mainly as a binder in many pharmaceutical tablets, being completely inert to human; it simply passes through the body when taken orally. PVP binds to polar molecules exceptionally well, owing to its polarity. This has led to its application in coatings for photo-quality inkjet papers and transparencies, as well as in inks for inkjet printers and a host of other technical applications. PVP find enormous use in pharmaceutical, biomedical and industrial applications (Selvakumar *et al.*, 2008). Semi-empirical theoretical methods (PM3 and AM1) are specially designed to obtain enthalpy of formation of chemical systems. AM1 and PM3 (Klein *et al.*, 2006; Kalnins, 2001) methods have been widely employed in structure, molecular geometry, FTIR, bond length, electrostatic potential and molecular orbital calculations and represent a standard tool for both theoretical and experimental organic chemists (Mertins and Dimova, 2011). We have selected PM3 and AM1 methods to compute, because these methods are fast enough to obtain results of the calculation in minute scales using an ordinary PC. The purpose of the present work was to determine the structure, molecular geometry, FTIR, bond length, electrostatic potential and molecular orbital of chitosan and PVP oligomers using PM3 and AM1 method, respectively.

II. METHODS

The analysis of the structure of chitosan used software Hyperchem software 8v using molecular mechanics and semi-empirical methods were generated.

The ground-state geometry of studied molecules was optimized at restricted Polak-Ribiere level and the geometry of the corresponding radicals was optimized at the restricted Polak-Ribiere open shell (half electron) level using the standard semi-empirical PM3 and AM1 methods of the HyperChem program package (energy cut-off of 10-5 kJ/mol, final RMS energy gradient under 0.01 kJ/mol Å) (Mertins and Dimiva, 2011). The FTIR results of the chitosan and PVP oligomers with PM3 and AM1 method were show in Tables 1-2, respectively. The orbital HOMO and LUMO molecular were obtained through the beta position for PM3 and AM1, this

analysis have been carried out to explain the charge transfer within molecule (Shihab, 2010).

III. RESULTS

A. Molecular geometry

Figure 3 shows the optimum geometry of an fraction of polymers (Chitosan-PVP) using (a) PM3 and (b) AM1 method, in where it is observed that the Gibbs free energy was -9028 and -5796 Kcal/mol, respectively; and the electrostatic binding of chitosan is energetically favorable (Gayathri and Arivazhagan, 2012). Attractive interactions between π systems are one of the principal non-covalent forces governing molecular recognition and play important roles in many chemical systems. Attractive interaction between π systems is the interaction between two or more molecules leading to self-organization by formation of a complex structure which has lower conformation equilibrium than of the separate components and shows different geometrical arrangement with high percentage of yield (Jindal *et al.*, 2013). The results confirm that the Gibbs free energy is spontaneous in both oligomers, due to be performed an attraction by hydrogen bond between the carbonyl group of the PVP and the OH group of chitosan (Yuan *et al.*, 2013).

B. Structural properties

The analysis computational was to determine the optimized geometry of chitosan-PVP. The molecular structure along with numbering of atoms as is shown in Fig. 3. The optimized structure parameter of chitosan-PVP (fraction of polymer) calculated PM3 and AM1 are listed in Tables 3-4, respectively, in accordance with the atom numbering scheme given in Fig. 3.

For the title molecules (chitosan-PVP), the structure is not planar and according to their observations, deformations of the ring depend on the characteristics of the substituents (OH, NH_2 , and $\text{CH}_2\text{-CH}_2$). Therefore, we could compare the calculation results given in Tables 3-4 with experimental data. As discussed the previous literature, several authors (Lertsuthiwong *et al.*, 2012) have explained the changes in frequency or bond length of the C-H bond on substitution due to a change in the charge distribution on the carbon atom of the ring. The substituents may be either of the electron withdrawing type (Cl, Br, F, etc.) or electron donating type (CH_3 , C_2H_5 , etc.).

The carbon atoms are bonded to the hydrogen atoms with an σ bond in ring and substitution of halogen for hydrogen reduces the electron density at the ring carbon atom. The ring carbon atoms shows a larger attraction on the valence electron cloud of the hydrogen atom resulting in an increase in the C-H force constant and a decrease in the corresponding bond length. The reverse holds well on substitution with electron donating groups. The actual change in the C-H bond length would be influenced by the combined effects of the inductive-mesmeric interaction and the electric dipole field of the polar substituent. The calculated geometric parameters can be used as foundation to calculate the other parameters for the compound.

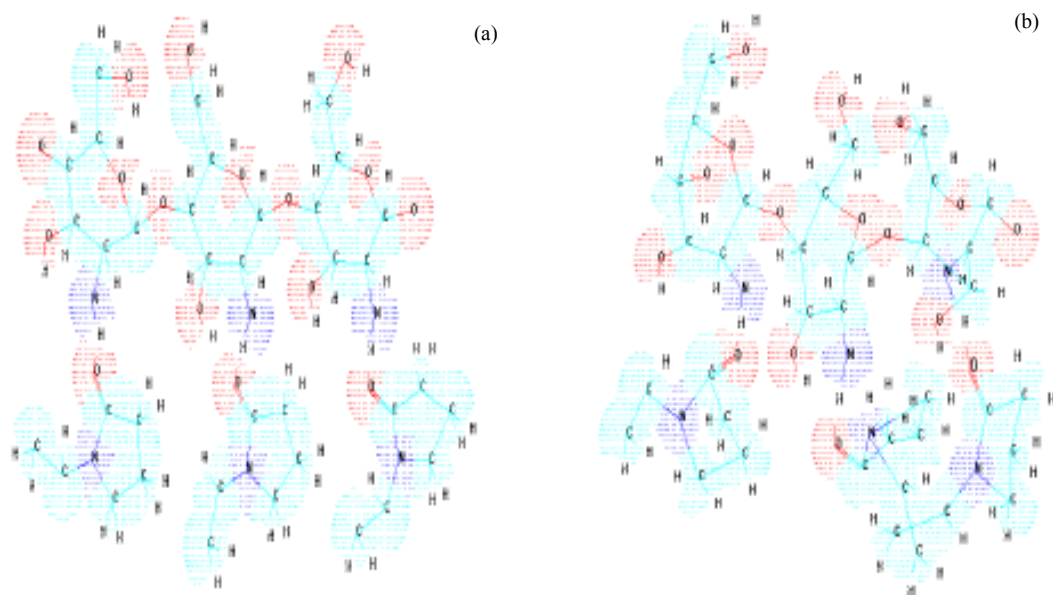


Fig. 3 Molecular geometry and structure of chitosan/PVP using (a) PM3 and (b) AM1 methods

Table 3. Structural parameters calculated for PVP employing PM3 and AM1 methods in chitosan/PVP (fraction of polymer)

Bond length (Å)	PM3	AM1	Bond length (Å)	PM3	AM1	Bond length (Å)	PM3	AM1
C4 – H1	1.09	1.10	C9 – H14	1.07	1.09	C23 – C24	1.58	1.62
C4 – H2	1.07	1.05	C9 – H15	1.09	1.05	C24 – C25	1.66	1.60
C4 – H3	1.14	1.10	C10 – H16	1.09	1.05	C25 – C26	1.58	1.55
C4 – C5	1.68	1.73	C10 – H36	1.09	1.07	C26 – N22	1.60	1.61
C5 – H6	1.00	1.03	C11 – O35	1.00	1.07	C23 – H27	1.07	1.09
C5 – N7	1.65	1.67	C5 – C17	1.67	1.69	C23 – H28	1.08	1.06
N7 – C8	1.88	1.90	C17 – H18	1.03	1.04	C24 – H29	1.03	1.06
C8 – C9	1.70	1.73	C17 – H19	1.05	1.04	C24 – H30	1.09	1.06
C9 – C10	1.67	1.68	C17 – C20	1.63	1.65	C25 – H31	1.09	1.07
C10 – C11	1.55	1.56	C20 – H21	1.00	1.02	C25 – H32	1.11	1.09
C8 – H12	1.03	1.01	C20 – N22	1.63	1.66	C26 – O33	1.21	1.25
C8 – H13	1.10	1.06	N22 – C23	1.55	1.58	O33 – H34	1.00	1.06

Table 4. Structural parameters calculated for chitosan employing PM3 and AM1 methods in chitosan/PVP (fraction of polymer)

Bond length (Å)	PM3	AM1	Bond length (Å)	PM3	AM1	Bond length (Å)	PM3	AM1
C1 – C2	1.43	1.49	O23 – C24	1.48	1.45	O43 – C45	1.44	1.45
C1 – C3	1.67	1.68	C24 – C25	1.69	1.66	C45 – C46	1.80	1.83
C3 – C4	1.69	1.69	C25 – O26	1.53	1.55	C46 – O47	1.66	1.68
C4 – C5	1.65	1.66	O26 – C27	1.61	1.60	O47 – C48	1.64	1.68
C5 – C6	1.64	1.66	C27 – C28	1.67	1.66	C48 – C49	1.92	1.72
C6 – O2	1.48	1.53	C28 – C29	1.73	1.68	C49 – C50	2.00	1.84
C1 – C7	1.57	1.57	C29 – C24	1.68	1.68	C50 – C45	1.92	1.88
C7 – H8	1.07	1.05	C24 – H36	0.88	0.92	C46 – C51	1.54	1.60
C7 – H9	1.09	1.05	C25 – H35	0.97	0.95	C51 – H52	1.00	1.01
C7 – O10	1.40	1.44	C29 – O37	1.40	1.42	C51 – H53	1.07	1.01
O10 – H11	0.96	1.00	O37 – H38	0.96	1.00	C51 – O54	1.40	1.43
C3 – H14	1.08	1.09	C29 – H39	1.09	1.03	O54 – H55	0.96	1.03
C3 – O12	1.44	1.45	C28 – N40	1.51	1.48	C45 – H56	1.06	1.09
O12 – H13	0.94	1.00	N40 – H41	0.97	1.00	C50 – O57	0.98	1.01
C4 – H20	1.08	1.09	N40 – H42	1.02	1.00	O57 – H58	0.86	0.93
C4 – O21	1.44	1.52	C27 – O43	1.45	1.48	C46 – H59	1.00	1.01
O21 – H22	0.95	0.97	C28 – H44	1.06	1.02	C49 – H60	1.00	1.01
C5 – H19	1.03	1.01	C27 – H68	1.09	1.03	C49 – N61	1.53	1.55
C5 – N16	1.56	1.58	C25 – C30	1.56	1.55	N61 – H62	1.00	1.04
N16 – H17	1.00	1.01	C30 – H31	1.07	1.10	N61 – H63	1.00	1.04
N16 – H18	1.02	1.04	C30 – H32	1.09	1.10	C50 – H64	1.09	1.07
C6 – H67	1.02	1.03	C30 – O33	1.41	1.43	C48 – O65	1.42	1.43
C6 – O23	1.45	1.43	O33 – H34	0.96	1.00	O65 – H66	0.95	1.00

C. Vibrational spectra

As both high molecular weight blend components contain proton donor (chitosan, OH) and proton acceptor

(PVP, C=O) groups, they may appear to be miscible, due to the hydrogen bond formation.

Thus, the FTIR spectra of film blends, in the car-

bonyl stretching region of PVP between 2107 at 2071 cm^{-1} , and the hydroxyl stretching bands of chitosan near 3477 cm^{-1} have been analyzed. FTIR peaks of chitosan-PVP (fraction of polymer) are presented in Table 5.

The absence of a band at 1650 cm^{-1} in the blend may be because water bonds to the interaction sites, thus preventing the strong interactions with chitosan and allowing PVP to the self-associations interactions more readily (Demirci *et al.*, 2009).

The intensity of some bands within the range 1500–1700 cm^{-1} that are related to amino and carbonyl moieties evidenced that these groups interact mainly through electrostatic interactions and hydrogen bonding.

At 3477 cm^{-1} was assigned to C-H and O-H stretching bands of chitosan. The band in 3185 cm^{-1} and shifting of band to lower wave number clearly indicates strong intermolecular interactions between chitosan and PVP. When the PVP oligomers is blended with chitosan, this absorption signal, which is assigned to the stretching vibration of a C=O group in the pyrrolidone ring, tends to shift to a position of somewhat lower frequency. These observations of frequency shifts for hydroxyl and carbonyl signals may be interpreted as due to the formation of hydrogen bonds between OH groups of chitosan and C=O groups of PVP. We noticed similar changes also for chitosan in its amine form. The shift of hydroxyl groups in the oligomers indicates that the miscibility of chitosan with PVP (Anupama and Wanchoo, 2012).

D. Molecular Electrostatic Potential

Molecular electrostatic potential (MESP), which is related to the electronegativity and the partial charge changes on the different atoms of the chitosan and PVP, when plotted on the density surface MEPS mapping is very useful in the investigation of the molecular structure with its physiochemical property relationships. Figure 4 shows the molecular electrostatic potential of chitosan-PVP (fraction of polymer) obtained through (a) PM3 and (b) AM1, respectively. Where can be seen in Fig. 4(a) -0.055 to 0.253 eV potential value, indicating that the structures presents electron-rich areas (pink color), while in Fig. 4(b) the value of the potential is -0.330 to 0.073 eV, by what can be seen that a large part of the

structures present a neutral potential (purple color), however electrophilic areas are located mainly in links C-OH, C=O and NH_2 , appreciates that the AM1 method unlike the positive potential decreases with respect to PM3 due to the complexity of the method used. Risbud *et al.* (2000a) have synthesized chitosan-PVP hydrogels and demonstrated their suitable properties and in vitro biocompatibility for biomedical applications. Addition of PVP to chitosan results in hydrogels with superior properties to unmodified chitosan in respect to mechanical strength, hydrophilicity and water content (Risbud and Bhat, 2001; Risbud *et al.*, 2000b). Chitosan-PVP hydrogels were seen to be highly hydrophilic as determined by the octane contact angle. Their increased hydrophilicity over unmodified chitosan is due to the presence of PVP, which is known to be highly hydrophilic (Howard, 1988). Though more hydrophilic than unmodified (Risbud *et al.*, 2000b)

E. HOMO and LUMO orbitals

Hydrogen bonding, electrostatic interactions, van der Waals interactions (van der Waals bonds are mainly constructed with a balance of the exchange repulsion and dispersion attractive interactions), donor-acceptor interactions, hydrophilic-hydrophobic interactions, and π - π interactions are the main types of non-covalent interactions that are responsible for self-organization in

Table 5. The calculated FTIR frequencies Chitosan/PVP (fraction of polymer) using PM3 and AM1.

Assignment	PM3 (frs. cm^{-1})	AM1 (frs. cm^{-1})
CH (CH_2 -OH) stretching	4375	4323
OH and CH (CH_2 -OH)	3477	3477
CH (CH_2 -OH) stretching	3458	3445
OH (CH_2 -OH chitosan)	3379	3362
OH (C-OH chitosan)	---	3315
CH (chitosan and PVP ring)	3215	3185
C-C (CH_3 - CH_2 PVP) stretching	2234	2205
C=O (PVP)	2107	2071
C-N (chitosan)	1942	1932
C-C (chitosan)	1889 – 1581	1870 – 1564
C-N (PVP)	1512	1484
C-O (chitosan ring)	1496	1475
C-O, C-C, C-N (chitosan and PVP)	1353 – 1285	1348 – 1266
NH_2 , C-H	1209	1188
C-H	671	645
OH	433	427

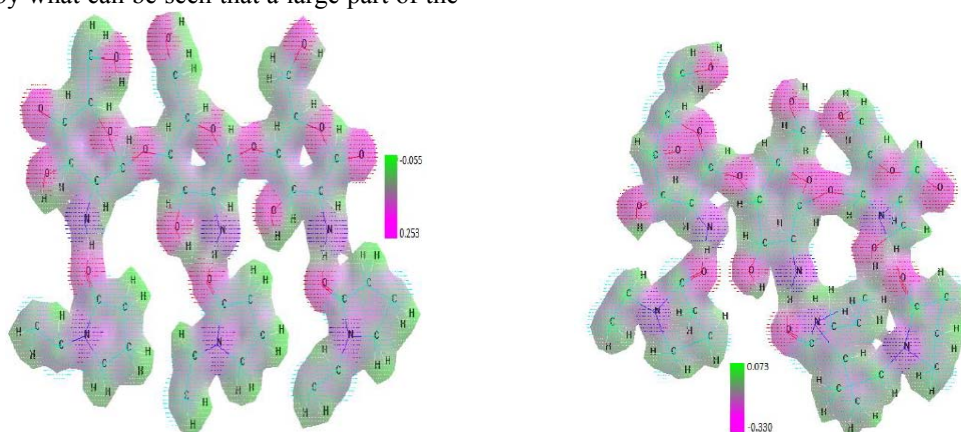


Fig. 4 Electrostatic potential of chitosan/PVP (fraction of polymer) using (a) PM3 and (b) AM1 methods

Table 6. HOMO and LUMO for chitosan/PVP (fraction of

polymer) using PM3 and AM1 methods

Method	PM3		AM1	
	HOMO	LUMO	HOMO	LUMO
Orbital	Energy (eV)	Energy (eV)	Energy (eV)	Energy (eV)
50	-14.85	3.54	-17.43	5.075
20	-11.43	1.64	-13.41	3.096
10	-10.21	0.43	-11.32	1.322
5	-09.56	0.11	-9.940	0.973
-5	0.0095	-9.50	0.957	-9.940
-10	0.3999	-10.19	1.273	-11.101
-20	1.33	-11.41	2.669	-13.265
-50	3.37	-14.76	5.072	-17.132

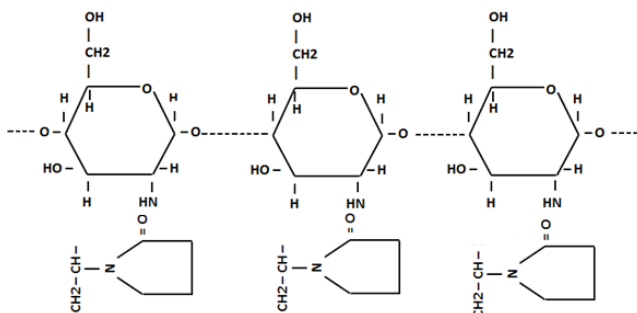


Fig. 5. Proposed structure of the Chitosan/PVP (fraction of polymer).

biological systems. An evidence of charge transfer (CT) complexes had been reported in solid or in solution in a different field of chemistry. The basic electronic parameters related to the orbitals in a molecule are the HOMO and LUMO (energy) of chitosan/PVP (fraction of polymer) can give us idea about the ground and excited state proton transfer processes.

The HOMO and LUMO energy calculations (see Table 6) reveal the existence of interactions and according to Mulliken's theory, formation of the (CT) complex involves transition of an electron from HOMO of donor to LUMO of acceptor. Opposing π systems typically adopt parallelplaner (stacked or offset-stacked) geometry. The interaction between the donor and acceptor is characteristic of an electronic absorption band with low energy. One of these molecular complexes is π,π -complex between neutral molecules (Shihab, 2010). Figure 5 shown structure proposed of the fraction of polymer (Chitosan-PVP), where is appreciated that the CH group of the PVP reacts with the amine groups of the Chitosan to generate the Chitosan/PVP. This fact suggests that interaction processes may be taking part in this region, differently from what occurs in the region of the amine group of the chitosan

IV. CONCLUSIONS

FTIR analyses showed the characteristic functional groups of the oligomers. The bond lengths are found to be almost same at PM3 and AM1 levels. For the title molecules, chitosan and PVP oligomers are not planar and according to the observations, deformations of the rings depend on the characteristics of the substituents (OH, NH₂, and CH₂-CH₂). The geometric parameters can be used as the basis to calculate the other parameters for the compound. HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. MESP plays an important role in determining stability of the molecule. The lone

pair electrons which provide stabilization to the molecular structure enhance its bioactivity. This study demonstrates that scaled calculations are a powerful approach for understanding the vibrational spectra of oligomers and fraction of polymer, respectively

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