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Geometrical structure, vibrational spectra and thermodynamic properties of chitosan constituents by DFT method

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Abstract: The interaction between glucosamine molecules has been studied theoretically. The geometrical structures of monomer (A), dimer (AA) and trimer (AAA) molecules of glucosamine were optimized and vibrational spectra were calculated by DFT/B3LYP method using GAMESS software (Firefly version 8.0.0). The theoretical vibrational spectra for the glucosamine dimer and trimer correspond well to the experimental IR spectrum of chitosan. The energies and enthalpies of association of A to form the dimer and trimer have been determined. The enthalpies of dimerization, $A + A = AA + H_2O$, and trimerization, $AA + A = AAA + H_2O$, are −48 and −45 kJ/mol, respectively. The thermodynamic functions of the monomer, dimer, and trimer molecules of glucosamine have been calculated.

Keywords: Glucosamine, Glucosamine Oligomers, Chitosan, DFT, Hydrogen Bond

1. Introduction

The physical and chemical properties of compounds are attributable to their structural parameters and also the energy of the complexes. Experimental measurement of the structural parameters is limited due to the expenses and facilities that can give results with accurate precision. Computational molecular modeling has greatly accelerated success in the determination of structural parameters, vibrational frequencies, and also thermodynamic properties of complexes. As a modern technique of chemistry, its advent and popularity in the last several decades and improvements in the computing power help chemists to predict molecular structure, interactions and properties and eventually understand chemical reactions and processes.

Chitosan is a natural polysaccharide found in crabs, shrimps, lobsters, corals, jellyfish, butterflies, ladybugs, mushrooms and fungi. Marine crustaceans shells are widely used as primary sources of chitin [1]. Chitin is regarded as the second most abundant polymer that exists in nature after cellulose [2]. It is formed from the repeating units of acetylglucosamine and glucosamine that link to form a large polymer unit. It is made up of a β(1-4)-linked 2acetamido-2-deoxy-β-D-glucose (N-acetylglusosamine) [3]. Chitosan is a derivative of chitin polysaccharides consisting of varying amounts of β(1-4)-linked residues of N-acetyl-2 amino-2-deoxy-D-glucose [4]. It has a similar structure as the chitin but the difference between them is the deacetylation degree and their respective solubility in dilute acidic media [5, 6]. A schematic chemical structure of a chitosan polymer is shown in Fig. 1.

Previously computation molecular modeling had been applied in the investigation of the interaction mechanism of chitosan constituents and heavy metals [7-9]. The aim of this work was to study the interaction between glucosamine molecules resulting in the dimer and trimer formation. The DFT method was applied to determine the structural parameters, vibrational spectra and thermodynamic properties of glucosamine oligomers.
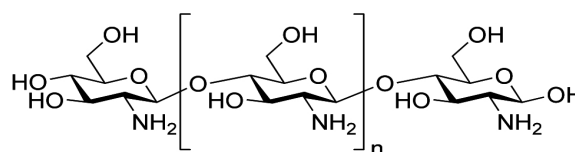

Figure 1. Schematic chemical structure of a deacetylated chitosan polymer.

2. Computational Methods

The chitosan constituents considered in this study are denoted as A for the monomer, AA for the dimer and AAA for the trimer glucosamine molecules. The structural parameters of the A, AA, and AAA have been obtained using electron density functional theory (DFT) with the Becke–Lee–Yang–Parr functional (B3LYP) and polarized split-valence basis set 6-31G(d, p). Firefly Quantum Chemical package, version 8.0.0 [10] which is partially based on the GAMESS (US) source code [11] has been used. Firefly as a versatile computation package allowed us to determine the equilibrium structure, *i.e.* a structure that represents a minimum on a potential energy surface. With this calculation, the internal coordinates such as the internuclear distances, valence angles and the torsion angles, were obtained. This process was followed by a hessian calculation to calculate the vibrational spectra. In this step, the vibrational frequencies and IR intensities were computed.

To display 3-D molecular structures and normal vibrational modes, the molecular visualization program wxMacIPlt [12] was used. Energies of the dimerization and trimerization reactions were computed using different basis sets: 6-31G(d,p), 6-31G++(d,p), and 6-311G++(d,p), the geometrical structures optimized with the basis set 6-31G(d,p) being used.

3. Results and Discussion

3.1. Equilibrium Geometrical Structures

The optimized geometrical structures of A, AA and AAA glucosamine molecules, presented in Figs. 2 (a), (b), (c), all belong to the C_1 point group symmetry. The most important selected geometrical parameters, namely the bond lengths, valence angles and torsion angles, are summarized in Tables 1–3.

(*a*)   (*b*)

(*c*)
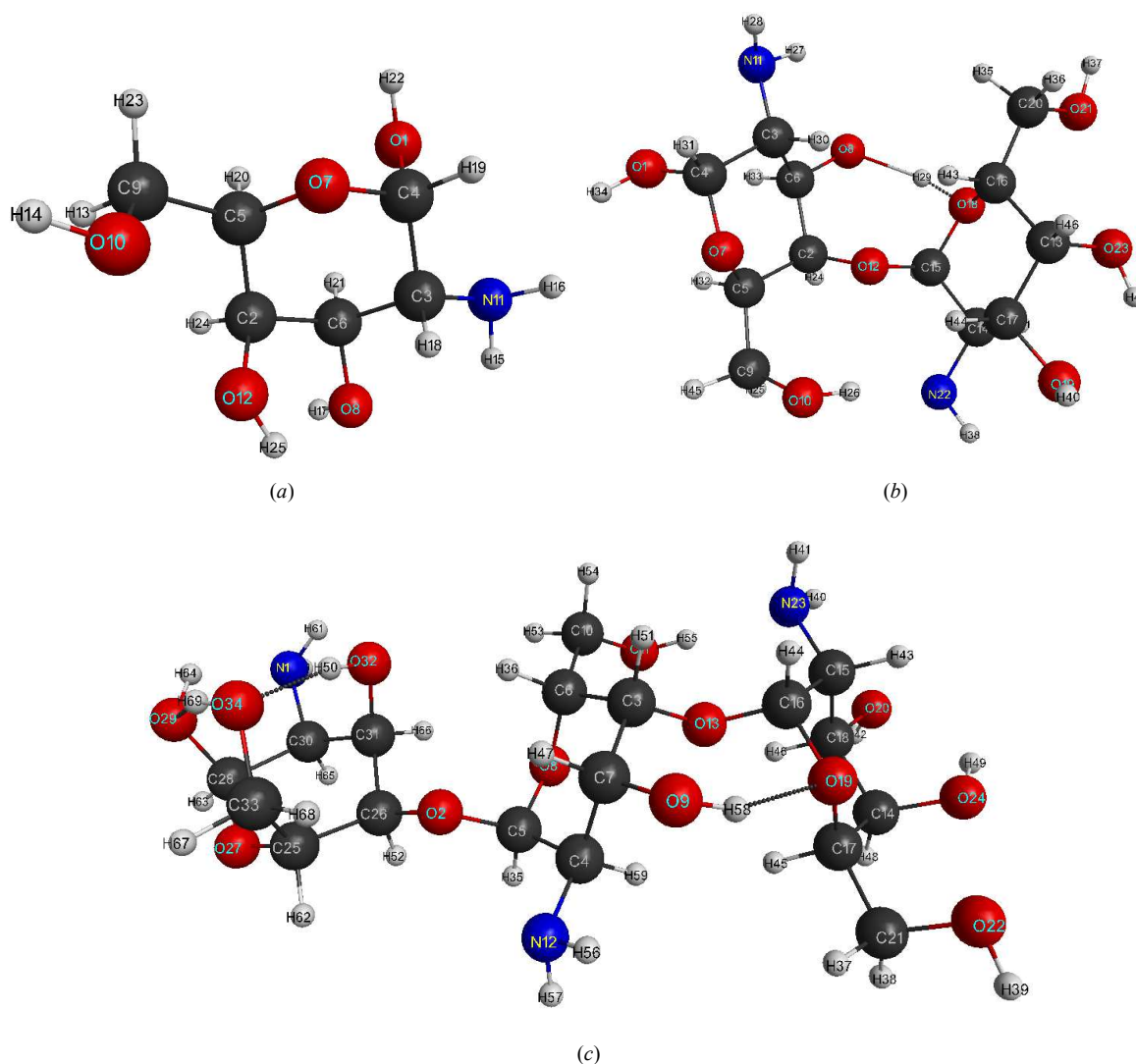
Figure 2. *Equilibrium geometrical structure of the glucosamine molecules: monomer A (a) A, dimer (b), and trimer (c).*

Each of the glucosamine molecules has six-atomic cycle with a ring oxygen atom inserted. All of these cycles in A,

AA, and AAA are not planar, as the sum of all six valence angles within the ring is much less than 720°; the values of

the torsion angles confirm non-planarity of the cycles as well. In the monomer A, the ring oxygen atom is attached between C4 and C5 making an angle C4-O7-C5 equal to 114°. In the dimer molecule AA, the corresponding angles, C4-O7-C5 and C15-O18-C16 are also both equal to 114°. In the trimer AAA, the similar angles are a bit different i.e.: 111° in the central ring, 112°, and 115° in the side rings. The two C-O internuclear distances regarding this C-O-C fragment are not equivalent; one is ~1.42 and the other is ~1.44 Å.

In the dimer and trimer molecules the cycles are linked by the glycosidic bond C-O-C. As it is noted in [13] this bond is responsible for the stiffness and stability of the chitosan molecular structure. Both in AA and AAA, the two C-O internuclear distances are not equivalent within the same C-O-C fragment in the glycosidic bond. The shortest is about 1.40 Å whereas the longest between 1.42–1.44 Å. In AA the valence angle C2-O12-C15 is 119° and the corresponding torsion angle C2-O12-C15-C14 is 138°. In AAA, the valence angles ∠C16-O13-C3 = 119° and ∠C5-O2-C26 = 117°; the torsion angles are 139° and 146° for C3-O13-C16-C15 and C5-O2-C26-C25 fragments respectively. In the trimer molecule, the glycosidic bridges are bent opposite to each other.

The -NH$_2$ group is attached to the ring carbon atom and is located at the opposite side with respect to the -CH$_2$OH group in each of the cycles of A, AA, and AAA molecules.

That is due to the mutual repulsion of both negatively charged N (q_N = −0.60) and O (q_O = −0.50) atoms in the -NH$_2$ and -CH$_2$OH group, respectively. In the neighboring rings of the dimer and trimer molecules, the amino groups occupy the opposite position to each other. It is generally accepted and remarkable to mention here that the amino groups of chitosan are responsible for its complexing with metal ions as the cations have a preference to ligands with the amino groups.

The average C-C bond length in the monomer A is 1.535 Å A, 1.540 Å in the dimer AA and 1.565 Å in the trimer AAA molecule. These results show that there is a slight increase in C-C separation between two atoms of the rings as the polymer increases in complexity. Similar results were obtained by Liu and co-workers in their investigation of N-Acetyl-D-glucosamine [14]. The internuclear distance C-N in A C3-N11 (1.461 Å) is comparable to C-N bond in AA C3-N11 (1.457 Å), C14-N22 (1.467 Å) and in AAA C30-N1 (1.472 Å), C4-N12 (1.459 Å), C15-N23 (1.466 Å). It appears that AAA has a bit longer averaged C-N bond length compared to AA and A. Another bond which may be considered is the O-H bond. In the monomer A the O-H bond length ranges from 0.965 to 0.971 Å, in AA the range is 0.965-0.981 Å, in AAA it is 0.969-0.991 Å. The averaged value of O-H internuclear separation is slightly increased again from A to AAA.

Table 1. *Geometrical parameters of the glucosamine monomer molecule A.*

Internuclear distance, R_e, Å		Valence angle, deg.		Torsion angle, deg.	Valence angle, deg.
C4-O7	1.414	C4-O7-C5	113.9	C2-C5-O7-C4	57.9
C5-O7	1.431	C4-C3-C6	109.2	C3-C4-O7-C5	−59.8
C2-C5	1.536	C2-C6-C3	110.7	C6-C2-C5-O7	−52.8
C2-C6	1.543	C5-C2-C6	109.3	C2-C6-C3-C4	−55.1
C3-C4	1.537	C2-C5-O7	112.3	C2-C5-C9-O10	67.7
C3-C6	1.523	C3-C4-O7	110.8	C2-C6-C3-N11	−178
C6-O8	1.44	C3-C6-O8	106.8	O12-C2-C6-O8	46.7
C2-O12	1.412	C6-C2-O12	109.6	C3-C6-C2-C5	52.6
C5-C9	1.524	C5-C2-O12	112.1	C3-C6-C2-O12	−70.6
C3-N11	1.461	O1-C4-O7	112.0	C6-C2-C5-O8	−52.8
C-H	1.104	C4-C3-N11	111.9	O7-C4-C3-C6	57.7
O-H	0.967	C2-C5-C9	116.5		

Note: The averaged bond lengths are: R_e(C-H) = 1.104; R_e(O-H) = 0.967; R_e(N-H) = 1.017 Å.

Table 2. *Geometrical parameters of the glucosamine dimer molecule AA.*

Internuclear distance, R_e, Å		Valence angle, deg.		Torsion angle, deg.	Valence angle, deg.
C4-O7	1.419	C4-O7-C5	113.7	C2-C5-O7-C4	60.4
C5-O7	1.433	C4-C3-C6	109.7	C3-C4-O7-C5	−60.8
C15-O18	1.423	C15-O18-C16	114.2	C13-C16-O18-C15	56.4
C16-O18	1.440	C15-C14-C17	109.0	C14-C15-O18-C16	−59.0
C2-C5	1.535	C3-C6-C2	110.2	C2-C6-C3-C4	−53.2
C13-C16	1.536	C13-C17-C14	109.7	C14-C17-C13-C16	54.2
C3-N11	1.457	C4-C3-N11	112.2	O7-C4-C3-N11	177.6
C14-N22	1.467	C15-C14-N22	110.6	O18-C15-C14-N22	179.6
C2-O12	1.438	C2-O12-C15	119.1	C6-C2-O12-C15	−85.1
C15-O12	1.400			C2-O12-C15-C14	−138.1
O18···H29	1.929	O8-H29···O18	159.2	C2-O12-C15-O18	100.4

Note: The averaged bond lengths are: R_e(C-H) = 1.107; R_e(O-H) = 0.971; R_e(N-H) = 1.017 Å.

Table 3. Geometrical parameters of the glucosamine trimer molecule AAA.

Internuclear distance, R_e, Å		Valence angle, deg.		Torsion angle, deg.		Valence angle, deg.
C5-O8	1.413	C5-O8-C6	113.7	C5-O8-C6-C3	60.8	
C6-O8	1.440	C3-C7-C4	110.2	C4-C5-O8-C6	−60.5	
C16-O19	1.424	C16-O19-C17	114.3	C16-O19-C17-C14	56.1	
C17-O19	1.439	C14-C18-C15	109.7	C15-C16-O19-C17	−58.8	
C28-O27	1.400	C25-O27-C28	119.9	C25-O27-C28-C30	45.9	
C25-O27	1.439	C26-C35-C30	109.9	C26-C25-O27-C28	−52.1	
C3-C6	1.533	C3-C7-C4	110.2	C4-C7-C3-C6	53.4	
C14-C17	1.536	C14-C18-C15	109.7	C14-C18-C15-C26	−57.8	
C25-C26	1.541	C26-C31-C30	109.9	C26-C31-C30-C28	41.7	
C4-N12	1.459	C5-C4-N12	112.1	O8-C5-C4-N12	177.4	
C15-N23	1.466	C16-C15-N23	110.6	O19-C16-C15-N23	179.5	
C30-N1	1.472	C28-C30-N1	107.7	O27-C28-C30-N1	−162.2	
C5-O2	1.408	C5-O2-C26	116.9	C7-C3-O13-C16	−85.5	
C16-O13	1.398	C3-O13-C16	119.1	C3-O13-C16-O19	99.7	
C3-O13	1.439			C5-O2-C26-C31	−86.9	
O19···H58	1.923	O9-H58···O19	160.0	C26-O2-C5-C4	−160.3	
O29···H69	1.768	O34-H69···O29	153.1	C26-O2-C5-O8	76.3	
O34···H50	1.735	O32-H50···O34	163.0	C5-O2-C26-C25	146.4	

Note: The averaged bond lengths are: R_e(C-H) = 1.099; R_e(O-H) = 0.977; R_e(N-H) = 1.018 Å.

The important feature in the dimer and trimer molecules is the appearance of the hydrogen bonds O···H-O. There are two types of hydrogen bonds may be considered, the first one is between two glucosamine molecules (intermolecular hydrogen bond) and the second type is within the glucosamine molecule (intra-molecular bond). Intermolecular hydrogen bonds were found both in the dimer and trimer molecules. In the AA, this bond is O8-H29···O18, R_e(H29···O18) = 1.929 Å, ∠O8-H29···O18 = 169°. In the AAA, the bond O19···H58-O9, R_e(H58···O19) = 1.923 Å, ∠O19···H58-O9 = 160° has been found, it is between the central ring and right-hand side one as is seen in Fig. 2 (c). The intra-molecular hydrogen bonds have been disclosed in the trimer molecule, they were O34-H69···O29 and O32-H50···O34 with R_e(H69···O29) = 1.768 Å, ∠O34-H69···O29 = 153°; R_e(H50···O34) = 1.735 Å, ∠O32-H50···O34 = 163°, respectively. In Fig. 2 (c), these bonds are seen in the left-hand side ring. The other two rings of AAA do not possess the intra-molecular H-bonds. Neither monomer nor dimer has this type of bond. Thus the intra-molecular hydrogen bonds are shorter than intermolecular bonds by ~0.2 Å. According to the IUPAC definition of hydrogen bond [15] the X-H···Y angle is usually close to 180º. In our case the angles O-H···O are less than 180º due to the helicon structure of the glucosamine oligomers. Therefore the H-bond formation favors the linkage between the glucosamine molecules, and along with the bending of the H-bond leads to the twisting of the oligomer chain.

3.2. Vibrational Spectra

The vibrational spectra of the monomer, dimer, and trimer glucosamine molecules were determined for the optimized geometrical configurations, true energy minima confirmed by the absence of imaginary frequencies. The vibrational analysis was done regarding the most common functional groups and structural components found in the three optimized structures. The theoretical spectra represented in Fig. 3 show a similar pattern: the three regions with significant absorption intensities are observed. The first region corresponds to 100–1660 cm^{-1} for A; 80–1660 for AA, and 80-1690 for AAA. The second region is 2920–3070 for A, 2930–3080 for AA, 2940–3140 for AAA; and the third one is 3740–3830 for A, 3490–3830 for AA, and 3340–3760 cm^{-1} for AAA. As is seen each of these three regions is expanding slightly in series A − AA − AAA. Experimental IR spectra of chitosan was obtained in [16-20] for the range between 750 and 4000 cm^{-1}. According to the data reported, three main regions of absorption, ~750–1700 cm^{-1}, 2850–3000 cm^{-1}, and 3100–3700 cm^{-1} may be observed. In this connection, our findings for the glucosamine molecules are in agreement with the experimental spectra of chitosan [19].

In the theoretical spectra, the characteristic vibrational modes can be considered regarding the functional groups of glucosamine. For the monomer molecule, the most intensive vibrations are found in the first low frequency region and correspond to the torsion vibrations involving O, N, and C atoms. Whereas both for the dimer and trimer molecules, the

most intensive vibrations are observed in the third, high frequency, region and correspond to the stretching vibrations of the N-H, and O-H groups, involving H-bonds as well. The

result on the O-H frequencies in the dimer and trimer is in agreement with the experimental spectrum of chitosan, in
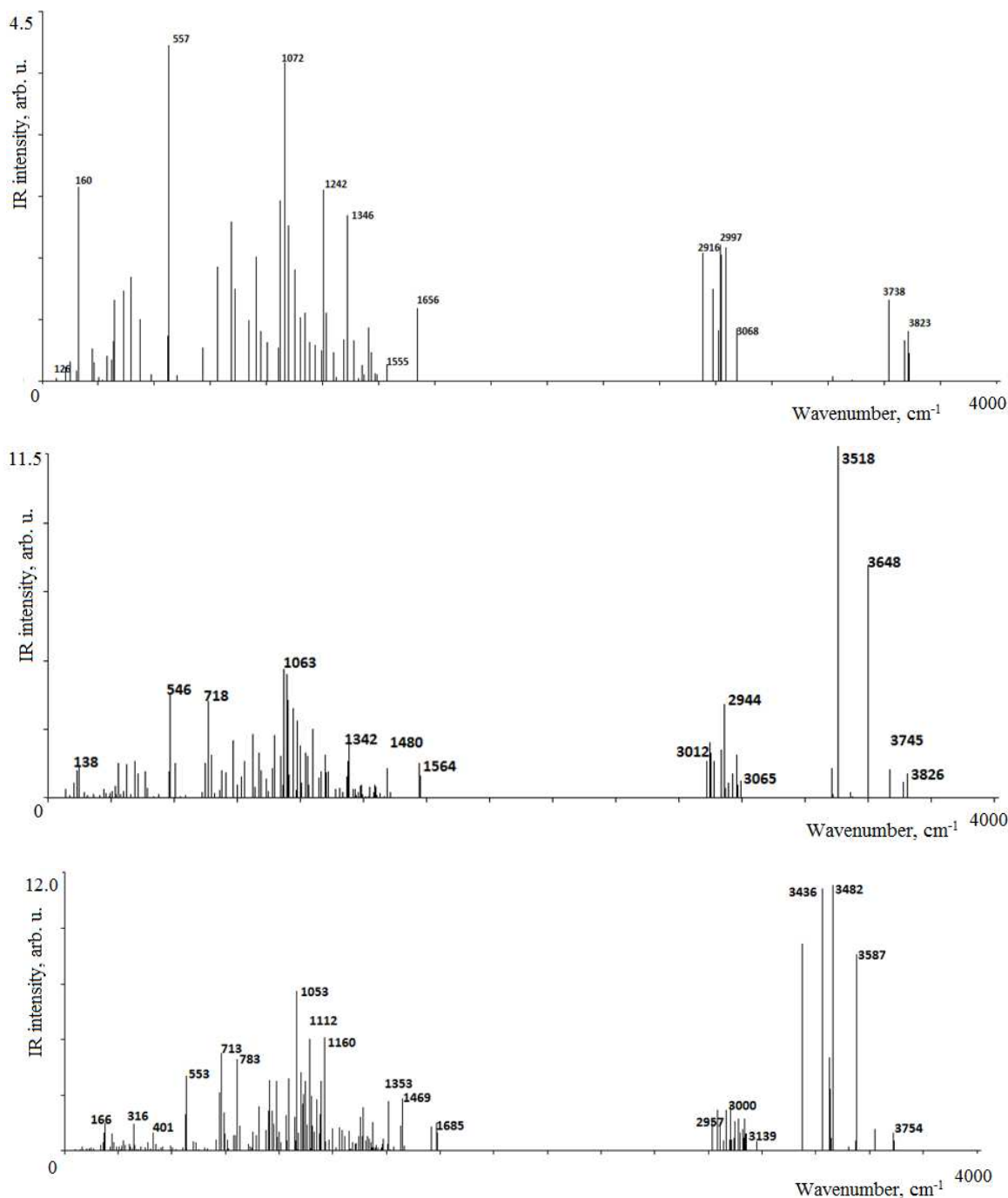
Figure 3. Theoretical IR spectra of the glucosamine molecules: monomer A (a); dimer AA (b), and trimer AAA (c).

which the most intensive and broad absorption band has been registered in the high frequency range with the peak at 3437.2 cm^{-1} for the O-H stretching mode [19]. The other characteristic frequencies in A, AA, and AAA may be underlined. The bending vibrations of the amino groups correspond to ~1660 cm^{-1} in all three molecules and it is in a

agreement with the experimental value of 1594 cm^{-1} [19], but the intensities in the theoretical spectra are lower compared to the experimental ones and may be due to higher concentration of NH$_2$-groups in the chitosan samples studied in [19].

***Table 4.** Thermodynamic functions of the glucosamine A, AA, and AAA.*

T, K	C°_{p}, J·mol^{-1}·K^{-1}	S°, J·mol^{-1}·K^{-1}	Φ°, J·mol^{-1}·K^{-1}	$H^{\circ}(T) - H^{\circ}(0)$, kJ·mol^{-1}
Monomer A				
298	208.16	452.32	333.21	35.49
300	209.29	453.71	334.01	35.91
350	237.44	488.10	353.58	47.08
400	264.41	521.58	372.48	59.64
450	289.52	554.20	390.88	73.49
500	312.48	585.91	408.81	88.55
550	333.25	616.68	426.30	104.71
600	352.00	646.50	443.43	121.84
Dimer AA				
298	386.17	662.92	450.51	63.30
300	388.43	665.51	451.94	64.07
350	444.37	729.47	486.91	84.90
400	497.81	792.47	521.31	108.46
450	547.41	854.01	554.87	134.61
500	592.61	914.06	587.80	163.13
550	633.40	972.49	620.13	193.80
600	670.12	1029.21	651.87	226.40
Trimer AAA				
298	555.13	880.42	580.01	89.52
300	558.5	884.15	582.02	90.64
350	642.08	976.55	631.80	120.66
400	722.04	1067.56	680.60	154.78
450	796.36	1156.95	728.57	192.77
500	864.16	1244.43	775.81	234.31
550	925.44	1329.71	822.30	279.08
600	980.64	1412.65	868.06	326.75

The second region of the spectra is assigned to the C-H stretching vibrations which is the same by the frequencies for monomer and dimer molecule but with a bit higher frequencies and broadening of the band for trimer. For CH$_2$ bend modes which appear in the first region, the frequencies are in the range 1479–1523 in A and AA, and a bit higher 1512–1539 cm^{-1} in AAA. This result of the increasing of stretching and bending vibrational frequencies in the trimer molecule can be explained in terms of the strengthening of the C-H bonds in the formation of AAA structure. This suggestion is supported by the decreasing of the averaged C-H bond in AAA by 0.005 Å compared to A or 0.008 Å compared to AA.

For the AA and AAA, the second spectral region contains as well the intensive modes about 1050 cm^{-1} which is assigned to C-O-C glycosidic bonds. Other intensive lines near 715 cm^{-1} are assigned to the deformational modes of H-O···H fragments with the hydrogen bonds. No such bands were noted in the experimental spectrum of chitosan. The difference between the theoretical and the experimental results may be attributed partially to difference in phases used. The experimental values are obtained for the solid phase while the theoretical values are computed for the gaseous phase of glucosamine.

3.3. Thermodynamic Functions

The thermodynamic functions of the momomer A, dimer AA, and trimer AAA glucosamine molecules were calculated on the base of the vibrational frequencies and optimized geometrical coordinates in the rigid rotator −

harmonic oscillator approximation using Openthermo computation package [21]. For temperature interval between 298−600 K, the molar heat capacity C°_{p}; the Gibbs reduced free energy Φ°; the entropy S°; and the enthalpy increment $H^{\circ}(T) - H^{\circ}(0)$ are listed in Table 4. The thermodynamic functions may be requested for the treatment of the experimental data on the evaporation of chitosan at elevated temperatures.

3.4. Association Reactions of Glucosamine Molecules

The association reactions of the glucosamine molecules resulting in the dimer AA and trimer AAA molecules have been considered. The reaction equations (I-III), the energies of the reactions $\Delta_r E$, zero point vibrational energy correction $\Delta ZPVE$ and enthalpies of the reactions $\Delta_r H^{\circ}(0\ K)$ are given in Table 5. The formation of the trimer molecule may be represented through the reaction (II) as the attachment of the monomer molecule to dimer or through reaction (III) as the association of three monomers. The third reaction is an auxiliary one, as it is in fact the combination of the first and second reactions.

The energies of the reactions were found trough the total energy of the products and reactants:

$$\Delta_r E = E_{prod} - E_{react} \tag{1}$$

The enthalpies of a reaction were calculated using the following equations:

$$\Delta_r H^{\circ}(0\ K) = \Delta_r E + \Delta ZPVE, \tag{2}$$

$$\Delta ZPVE = (1/2)hc(\Sigma\omega_{i\ prod} - \Sigma\omega_{i\ react}) \quad (3)$$

where $\Sigma\omega_{i\ prod}$, $\Sigma\omega_{i\ react}$ are the sums of the vibration frequencies of the products and reactants, respectively.

The results have been obtained using different basis sets, 6-31G(d,p), 6-31G++(d,p), 6-311G++(d,p). For the second and third basis sets the diffused functions have been added for the H, O, and N atoms. As is seen from Table 5, the both reactions for the dimer and trimer formations are exothermic. The implication of the diffuse functions brings to less negative values of the enthalpies of the reactions and the most remarkable change is observed for the trimerization reaction. So for the basis set 6-31G++(d,p), the change in the values of $\Delta_r H^o(0\ K)$ is ~6 kJ·mol^{-1} for the reaction (I) and 26 kJ·mol^{-1} for the reaction (II) compared to the results by the basis set 6-31G(d,p). The further extending of the basis set through the splitting does not give essential difference in the enthalpies of the reactions.

Table 5. *The reaction equations, energies $\Delta_r E$, zero point vibrational energy corrections $\Delta ZPVE$ and enthalpies $\Delta_r H^o(0\ K)$.of the reactions.*

No	Reaction	Basis set	$\Delta_r E$, kJ·mol^{-1}	$\Delta ZPVE$, kJ·mol^{-1}	$\Delta_r H^o(0\ K)$, kJ·mol^{-1}
I	$2A = AA + H_2O$	6-31G(d,p)	−52.2	−2.1	−54.3
		6-31++G(d,p)	−46.4	−2.1	−48.5
		6-311++G(d,p)	−45.6	−2.1	−47.7
II	$AA + A = AAA + H_2O$	6-31G(d,p)	−69.9	3.5	−66.4
		6-31++G(d,p)	−44.1	3.5	−40.6
		6-311++G(d,p)	−48.7	3.5	−45.2
III	$3A = AAA + 2H_2O$	6-31G(d,p)	−122.1	1.5	−120.6
		6-31++G(d,p)	−90.5	1.5	−89.0
		6-311++G(d,p)	−94.3	1.5	−92.8

The recommended values of $\Delta_r H^o(0\ K)$ according to the calculations in the most extended basis set 6-311G++(d, p) are −48 and −45 kJ·mol^{-1} for the reaction (I) and (II) respectively. This implies that attachment energies of the glucosamine molecule to the monomer or dimer are comparable. We suggest that the attachment of the next glucosamine molecule to the trimer will bring the further stabilization of the larger oligomers and facilitate molecular chain formation.

4. Conclusion

The equilibrium geometrical parameters were obtained by DFT/B3LYP method for the monomer, dimer, and trimer glucosamine molecules. In the dimer and trimer molecules, the glycosidic bond links two neighboring non planar six-atomic-cycles. The hydrogen bonds were shown to exist in the dimer and trimer molecules and favor the strengthening of the oligomers' structure. The calculated vibrational spectra with the typical characteristic modes of the functional groups of glucosamine were proved to be in accordance with the reference experimental spectra of the deacetylated chitosan. The enthalpies of the dimerization and trimerization reactions of the glucosamine molecules were found and it appeared that these values were comparable.

Acknowledgment

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