A Cyclic Periodic Wave Function Approach for the Study of Infinitely Periodic Solid-State Systems: II. Application to Helical Polysaccharides

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ABSTRACT: The cyclic periodic wave function (CPWF) approach is applied at the AM1 and PM3 semiempirical levels of approximation to two infinitely periodic polymer systems in the solid state. The two polysaccharides of interest here are (1→3)-β-D-glucan and (1→3)-β-D-xylan. Our calculated results show excellent agreement with the available data for the two polysaccharides and demonstrate that the use of the CPWF approach at the AM1 and PM3 levels of approximation provides a convenient and reliable method for the study of infinitely periodic bonds of two different types: moderately strong O···H···O hydrogen bonding and strong C···O···C covalent bonding.

1. INTRODUCTION

Quantum-mechanical computations at different levels of ab initio and semiempirical methods have been extensively applied to solve problems in many areas of chemistry, such as studying molecular periodic systems. Since the 1970s, the cluster models,1−3 cyclic cluster models (CCM),4−13 and pair-potential methods14−20 have been widely applied to study periodic molecular solid-state systems by using of Bloch orbitals,21 and density function theory (DFT).22,23 Along with the innovation of larger-capacity computers and the development of many software packages, such as the GAUSSIAN program,24 MOPAC25, the Vienna ab initio package (VASP),26−30 and the newly developed CRYSTAL31,32 and CRYSCOR33,34 programs, it is relatively easy to study the properties for many molecular periodic solid systems.35−39 However, applying any of the current quantum-mechanical methods to study large molecular systems, such as polymers with weak interactions, is still very challenging. In those large molecular systems, it is computationally demanding to study weak interactions due to the need to simultaneously use relatively large basis sets and high-order correlation corrections.40−42 We have solved some of these problems successfully by applying the cyclic periodic wave function (CPWF) method14 at the AM144 and PM345,46 semiempirical levels of approximation. Our calculation results for the study of infinitely periodic solid-state systems containing very weak CH···π (C−H···π) interactions between repeat units are submitted in the previous paper.47

Our goal in this paper is to continue applying this CPWF approach at the AM144 and PM345,46 semiempirical levels of approximation to systems containing weak interactions. Thus, we will use our modified MOPAC55 routines to study two infinitely periodic polysaccharides. These two polysaccharides are (1→3)-β-D-glucan and (1→3)-β-D-xylan, which involve both hydrogen bonds (O···H···O) and covalent bonds (C···O···C) between the repeat units. The conformations of these two polysaccharides are quite complex because of their multiple forms. (1→3)-β-D-Glucans, shown in Figure 1, are widespread in nature and participate in various types of biological responses.48−55 Several studies revealed the presence of different conformations for linear (1→3)-β-D-glucans, which include a single chain, single helix, triple helix, and random coil.55−65 The second polysaccharide, (1→3)-β-D-xylan, shown in Figure 2, is mainly found on the cell walls of a number of siphonophore green algae.66,67 It has a similar molecular structure to that of (1→3)-β-D-glucan, except that the equatorial hydroxymethyl group bonded to C(5) in the glucose residue of (1→3)-β-D-glucan is replaced with a hydrogen atom.

The three distinct conformations of a single chain, single helix, and triple helix have been found in (1→3)-β-D-xylan using 13C NMR spectroscopy.68,69 X-ray diffraction results show that both (1→3)-β-D-glucan and (1→3)-β-D-xylan have similar interplanar spacing and features.70−77 In addition, X-ray studies indicate that water is present in the lattice of (1→3)-β-D-xylan.66,69,74

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In this paper, we will first apply the CPWF approach at both the AM1 and PM3 levels of approximation to isolated single helices and triple helices, and then to the triple helical solid for (1→3)-β-D-glucan. Next, we will perform similar calculations on isolated anhydrous and hydrated single helices, isolated triple helices for (1→3)-β-D-xylan, and the three-dimensional triple helical solid of hydrated (1→3)-β-D-xylan based on the results from the calculations of (1→3)-β-D-glucan.

2. COMPUTATIONAL METHODS

We will apply the cyclic periodic wave function (CPWF) method, which has been described in detail in the previous paper.\(^4\) This method uses the full infinite Hamiltonian operator with a basis set composed from cyclic periodic wave functions, which use a molecular unit or monomer as the repeat unit rather than using the crystal unit cell.\(^4\) This gives a more chemically intuitive approach since the individual monomer will then provide the 0th-order form. The key to this method then rests in the form for the basis set functions, as is shown in eq 1.

\[
\psi_i = \psi_{I_1 I_2 I_3 N_1 N_2 N_3} = (N_1 N_2 N_3)^{-1/2} \sum_{I_1=0}^{N_1-1} \sum_{I_2=0}^{N_2-1} \sum_{I_3=0}^{N_3-1} \sum_{i_z=0}^{2\pi} e^{i(I_1 I_2 I_3)/2} \phi^\alpha_{I_1 I_2 I_3}(r)
\]

The expansion in eq 1 is dependent on the use of a three-dimensional indexing system, \((I_1, I_2, I_3)\), such that every repeat unit in the infinite crystal can be identified by its unique set of indices.

Next, the repeat length \(N_i\) in each direction is chosen. We will use \(N_1 = N_2 = N_3 = 4\) for the systems studied here. This ensures that all interactions within ±1 from the central unit will be treated exactly. These are considered to be the nearest-neighbor interactions. Interactions within ±2 or more will be included only electrostatically, as discussed in detail in the previous paper.\(^3\) Equation 1 ensures that the basis set functions, \(\psi_i\), are 4-fold periodic in each direction. \(\phi^\alpha_{I_1 I_2 I_3}\) are the atomic orbitals, which occur in the repeat unit at position \((I_1, I_2, I_3)\).

This approach will be applied at both of the AM1 and PM3 levels of approximation to the crystal structures of (1→3)-β-D-glucan and (1→3)-β-D-xylan. Since the space group for both the (1→3)-β-D-glucan triple helical solid and hydrated (1→3)-β-D-xylan triple helical solid is \(P6_0\), we will use the same spatial symmetry and indexing scheme for both solids in our calculations.

3. RESULTS AND DISCUSSION

3.1. (1→3)-β-D-Glucan. Our calculations started initially with the isolated 6/1-single helix of (1→3)-β-D-glucan. The glucose residue was selected as the repeat unit, and its experimental geometry\(^6\) was chosen as our initial molecular geometry. This ensures fast convergence in both molecular geometry and energy calculations. Since there was no experimental geometric data for the positions of the H atoms bonded to O(2), O(4), and O(6), we used typical O–H distances and C–O–H angles to generate the initial values of these parameters. Next, we varied all the geometric parameters for the 6/1-single helix until a minimum energy was found. In order to make sure our final energy was a global minimum and not just a local minimum, the three dihedral angles for the H atoms bonded to O(2), O(4), and O(6) were all varied step by step, while the other parameters remained at their previously optimized values. If a lower energy was found for a different set of dihedral angles, we then reoptimized all the geometry parameters to obtain a new energy minimum. This procedure was used at both the AM1 and PM3 levels of approximation.

The calculations for the one-dimensional triple helices were performed using the same steps as those for the single helices. To simplify the calculation, the repeat unit for the triple helices consists of three residues, one from each of three different strands. Both our initial molecular geometry and the initial value for the \(c\) cell dimension were chosen from the experimental geometry of the 6/1-triple helical solid.\(^5\) Comparing the differences in the heats of formation calculated for the triple helices and the corresponding single helices, we can estimate the binding energy between the strands of the triple helices as follows:
within the triple helix), is then calculated as follows:

\[ \Delta H_{H_{(1)}}^{IP,\text{(intra)}} = \Delta H_{f}(1) - 3 \times \Delta H_{f}(3) \]  

where \( \Delta H_{f}(1) \) is the heat of formation calculated for the triple helices and \( \Delta H_{f}(3) \) is the heat of formation calculated for the corresponding single helices. The intra-helix hydrogen bond energy, \( \Delta H_{H_{(1)}}^{IP,\text{(intra)}} \) (i.e., strand-to-strand hydrogen bond energy within the triple helix), is then calculated as follows:

\[ \Delta H_{H_{(1)}}^{IP,\text{(intra)}} = (1/3) \times \Delta H_{H_{(1)}}^{IP,\text{(intra)}} \]  

For the 6/1-triple helical solid of (1→3)-\( \beta \)-D-glucan, we used the identical form of the repeat unit as was used for the isolated triple helix. The calculations were performed using the same steps as those for the isolated triple helix, and our initial geometries were determined from our final results for the isolated 6/1-triple helix and from the experimentally determined cell dimensions.58

By comparing the differences in the calculated heats of formation between the triple helical solid and the corresponding isolated triple helix, we can estimate the binding energy between triple helices and the corresponding hydrogen bond energy. The binding energy \( \Delta H_{H_{(1)}}^{IP,\text{(inter)}} \) for the triple helical solid is thus determined as follows:

\[ \Delta H_{H_{(1)}}^{IP,\text{(inter)}} = \Delta H_{f}(t) - \Delta H_{f}(3) \]  

where \( \Delta H_{f}(t) \) is the calculated heat of formation for the triple helical solid and \( \Delta H_{f}(3) \) is the calculated heat of formation for the corresponding isolated triple helix. Since each repeat unit is involved in six hydrogen bonds, the inter-helix (i.e., triple helix to triple helix) hydrogen bond energy \( \Delta H_{H_{(1)}}^{IP,\text{(inter)}} \) for the three-dimensional triple helical solid is then calculated as follows:

\[ \Delta H_{H_{(1)}}^{IP,\text{(inter)}} = (1/6) \times \Delta H_{H_{(1)}}^{IP,\text{(intra)}} \]  

Our results are summarized in Tables 1–4 and Figures 3 and 4.

Table 1. Parameters of the Inter-helix Hydrogen Bonds for 6/1-Triple Helical (1→3)-\( \beta \)-D-Glucan Solids

| glucan solid | O–H–O | C–H–O |
|--------------|--------|--------|
|              | \( d_{ij} \) (Å) | \( \theta_{ij} \) (°) | \( d_{ij} \) (Å) | \( \theta_{ij} \) (°) |
| PM3          | O(6)–O(4) 3.0 | 106 | C(6)–O(6) 3.5 | 139 |
|              | O(6)–H–O(4) |  | C(6)–H–O(6) |  |
| AM1          | O(6)–O(4) 2.7 | 116 | C(6)–O(5) 3.8 | 148 |
|              | O(4)–H–O(4) 93 |  | C(4)–H–O(6) 3.8 | 137 |
|              | O(6)–O(6) 3.6 | 126 | C(6)–H–O(4) 3.9 | 148 |

Experimental data58

|              | O(6)–O(4) 2.71 |  | C(6)–O(4) 4.1 |  |
|              | O(6)–H–O(6) 3.05 |  | C(6)–H–O(4) 4.1 |  |
|              | O(6)–O(6) 2.75 |  | C(6)–O(5) 3.98 |  |

\( ^{a} \)Different O–O bond distances for O–H–O hydrogen bonds. \( ^{b} \)Different bond angles for O–H–O hydrogen bonds. \( ^{c} \)Different C–O bond distances for C–H–O hydrogen bonds. \( ^{d} \)Different bond angles for C–H–O hydrogen bonds.

\[ \Delta H_{H_{(1)}}^{IP,\text{(inter)}} = \Delta H_{f}(t) - \Delta H_{f}(3) \]  

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\[ \text{Our results are summarized in Tables 1–4 and Figures 3 and 4.} \]

Table 2. Interaction Energies of the Intra- and Inter-helix Hydrogen Bonds for the 6/1-Triple Helical Solids

| 6/1-triple helical solid | \( \Delta H_{H_{(1)}}^{IP,\text{(intra)}} \) (kcal/mol) | \( \Delta H_{H_{(1)}}^{IP,\text{(inter)}} \) (kcal/mol) |
|--------------------------|--------------------------|--------------------------|
| (1→3)-\( \beta \)-D-glucan |            |            |
| PM3                      | −8.82                    | −8.78                    |
| AM1                      | −1.24                    | −3.69                    |
| hydrated (1→3)-\( \beta \)-D-xylan |            |            |
| PM3 (conformation I)     | −2.27                    | −0.67                    |
| PM3 (conformation II)    | −2.32                    | −8.57                    |
| AM1 (conformation I)     | −1.83                    | −1.53                    |

\( ^{a} \)Intra-helix hydrogen bond energy. \( ^{b} \)Inter-helix hydrogen bond energy.

From Table 2, we see that the intra- and inter-helix hydrogen bond energies for glucan, calculated at the PM3 level of approximation, are −8.82 and −8.78 kcal/mol, respectively. These energies are −1.24 and −3.69 kcal/mol calculated at the AM1 level of approximation, both of which are considerably weaker than predicted by the PM3 calculations. From Table 1, we can see that the inter-helix interaction energies in each case
Table 3. Parameters of the Intra-helix Hydrogen Bonds for the 6/1-Triple Helical Solids

| 6/1-triple helical solid | O−H−O |
|--------------------------|-------|
|                          | d (Å) | θ (°) |
| (1→3)-β-D-glucan         |       |       |
| PM3                     | 3.1   | 91    |
| AM1                     | 2.9   | 104   |
| experimental data        | 2.72  |       |
| hydrated (1→3)-β-D-xylan |       |       |
| PM3 (conformation I)     | 3.0   | 107   |
| PM3 (conformation II)    | 2.9   | 94    |
| AM1 (conformation I)     | 2.9   | 105   |

*aO···O bond distance for the intra-helix O−H−O hydrogen bond. *bBond angle for the intra-helix O−H−O hydrogen bond.

Table 4. Unit Cell Parameters for the 6/1-Triple Helical Solids

| 6/1-triple helical solid | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) |
|--------------------------|-------|-------|-------|-------|-------|-------|
| (1→3)-β-D-glucan         |       |       |       |       |       |       |
| PM3                      | 14.7  | 14.7  | 5.6   | 90    | 90    | 120   |
| AM1                      | 13.9  | 13.9  | 5.7   | 90    | 90    | 120   |
| experimental data        | 14.41 | 14.41 | 5.87  | 90    | 90    | 120   |
| hydrated (1→3)-β-D-xylan |       |       |       |       |       |       |
| PM3 (conformation I)     | 15.4  | 15.4  | 5.8   | 90    | 90    | 120   |
| PM3 (conformation II)    | 13.8  | 13.8  | 5.7   | 90    | 90    | 120   |
| AM1 (conformation I)     | 15.3  | 15.3  | 5.8   | 90    | 90    | 120   |
| experimental data        | 15.4  | 15.4  | 6.12  | 90    | 90    | 120   |

*Errors are ±0.05.

are determined by more than a single type of interaction. In glucan, we find that both O−H···O and C−H···O types of interactions are important in stabilizing the structure. According to Steiner,75 the typical C−H···O bond energy is ≤2 kcal/mol and that for the typical O−H···O varies between 4 and 5 kcal/mol.76,77 If we take this into consideration, we would expect the AM1 calculations to have stronger total interaction energies than PM3 since there are some additional O−H···O and C−H···O contacts occurring in the AM1 structure. However, the PM3 calculations lead to stronger interaction energies than the AM1 calculations, and it appears that AM1 underestimates the stability of those hydrogen bonds.

From Tables 1 and 3, we see that the O(6)···O(4) bond length is 2.7 Å from AM1 and 3.0 Å from PM3, with AM1 giving closer agreement to the experimental value of 2.71 Å.58 The O(2)···O(2) bond length is 2.9 Å from AM1 and 3.1 Å from PM3. Once again the one from AM1 is somewhat closer to the experimental values of 2.72 Å for the intra-helix hydrogen bond.

Miyoshi et al.78 carried out cluster calculations using MOPAC and ab initio calculations, and proposed two conformations with different hydrogen bond forms for the (1→3)-β-glucan triple helix. The inter molecular hydrogen bond lengths between O(2)−O(2)’ are 3.3 Å for both conformations, and their calculated hydrogen bond energies are 2.6 and 3.1 kcal/mol, respectively.78 Their hydrogen bond energies are closer to our AM1 values, but both our AM1 and PM3 results give hydrogen bond lengths that are closer to the experimental values.

From Table 4, we see that the cell dimensions calculated at the AM1 and PM3 levels of approximation agree very well with those from the experimental data.58 PM3 gave somewhat better values for the a and b dimensions, and both AM1 and PM3 gave c values that were in excellent agreement with the experimental value.58

3.2. (1→3)-β-D-Xylan. We first performed the same calculations for anhydrous (1→3)-β-D-xylan as for (1→3)-β-D-glucan using the same steps to determine the optimal geometries. Since no experimental geometries exist for either the single or triple helices of (1→3)-β-D-xylan, we used our results from the 6/1-single and triple helices of (1→3)-β-D-glucan to set up the initial geometries for the corresponding one-dimensional (1→3)-β-D-xylan. Since cell dimensions have been reported for anhydrous (1→3)-β-D-xylan,66,79 we used the experimentally determined value for the fiber axis, c, as the initial value for the repeat length in the isolated helix. However, we discovered that no stabilization occurred between triple helices for the anhydrous 6/1-triple helical solid of (1→3)-β-D-xylan since only weak van der Waals interactions can provide stabilization between the triple helices, and AM1 and PM3 cannot properly model such interactions.

Next, we repeated this process on the hydrated (1→3)-β-D-xylan. For the single helices, the repeat unit consisted of one xylose residue and its mediated water molecule. For the triple helices and the triple helical solid of hydrated (1→3)-β-D-xylan, we chose the repeat unit to consist of three xylose residues, one from each of three different strands, each with its corresponding water molecule.

In modeling the hydrated form of xylan, it is very challenging to position the water molecules since there are multiple possible positions around the xylose residue where they can reside. Veluraja and Atkins74 suggested that the water-mediated interchain hydrogen bond is between the O(4) of residue n (chain II) and the O(5) of residue n + 1 (chain I) with equal distances of 2.8 Å. However, using their model, we were unable to obtain stable interaction energies between the triple helices since only weak van der Waals interactions would be available for inter-helix stabilization. Instead, we proposed a different model in which the oxygen in the water molecule was placed at the same position as the oxygen in the −CH₂OH group bonded to C(5) in the glucose residue in (1→3)-β-D-glucan. Thus, the water molecule was positioned so that it would provide a similar hydrogen bond interaction in xylose as that seen in glucan. That is, for our initial geometry, we assumed that the oxygen atom from the water molecule was “connected” with the oxygen atom O(4) in the residue with an initial distance of 2.8 Å. The only similarity between our model and the model proposed by Veluraja and Atkins74 is that the oxygen in the water molecule was placed at a distance of 2.8 Å from O(4) in the xylose residue. The major difference between the two models is that the water molecules in our model are linked through triads of hydrogen bonds with each other to stabilize the triple helical solid. Finally, we used the final molecular geometries from the 6/1-triple helical solid of (1→3)-β-D-glucan and the experimental unit cell parameters for the 6/1-triple helical solid of hydrated (1→3)-β-D-xylan66,79 to
determine the remaining initial geometry parameters for hydrated \((1\rightarrow 3)\)-\(\beta\)-D-xylan. Then, all geometric parameters were optimized until the geometry at the energy minimum was found.

In our calculations for hydrated \((1\rightarrow 3)\)-\(\beta\)-D-xylan solids, we obtained two different stable conformations, conformation I and conformation II, at the PM3 level of approximation and one stable conformation, conformation I, at the AM1 level of approximation. Conformation I is the form previously discussed and is shown in Figures 5 and 6, and conformation II is shown in Figures 7 and 8. The principal differences between these two conformations involve the inter-helix hydrogen bonds. In conformation I, there are two different kinds of inter-helix hydrogen bonds: \(\text{OW}^-\text{HW}1\cdots\text{OW}\) and \(\text{OW}^-\text{HW}2\cdots\text{O}(4)\) where the subscript W indicates that the atom belongs to the water molecule. In conformation II, there are also two different kinds of inter-helix hydrogen bonds, but these are \(\text{OW}^-\text{HW}2\cdots\text{O}(5)\) and \(\text{OW}^-\text{HW}2\cdots\text{O}(3)\). However, conformation II also has \(\text{C}^-\text{H}\cdots\text{O}\) contacts that are missing from conformation I. These involve close contacts between \(\text{C}(2)\) and \(\text{OW}\), \(\text{C}(3)\) and \(\text{OW}\), \(\text{C}(4)\) and \(\text{O}(4)\), and \(\text{C}(5)\) and \(\text{O}(4)\). These calculated results are shown in Table 2–5 and Figure 5–8.

The energy of hydration for the triple helix is calculated as follows:

\[
\Delta H_{(TH)} = \Delta H_{(thy)} - (\Delta H_{(tan)} + 3 \times \Delta H_{(water)})
\]

where \(\Delta H_{(TH)}\) is the total energy of hydration for the triple helix, \(\Delta H_{(thy)}\) is the calculated heat of formation of the hydrated triple helix, \(\Delta H_{(tan)}\) is the calculated heat of formation for its corresponding anhydrous triple helix, and \(\Delta H_{(water)}\) is the calculated heat of formation for the water molecule. The energy of hydration per xylose residue is then given by

\[
\Delta H_{(H)} = \frac{1}{3} \Delta H_{(TH)}
\]

Our results for the hydration energies are summarized in Table 6.

From Table 6, we see that the hydrated helices of xylan are predicted to be more stable than the corresponding helices of...
anhydrous xylan. Furthermore, we were only able to obtain stable crystal structures when water molecules were available to provide hydrogen bonding between triple helices. Thus, we will focus on our results from the hydrated xylans rather than those from the anhydrous form.

From Table 2, we see that the intra- and inter-helix hydrogen bond energies for hydrated xylan at the PM3 level of approximation are $-2.27$ and $-0.67$ kcal/mol for conformation I, and $-2.32$ and $-8.57$ kcal/mol for conformation II, respectively. The corresponding energies are $-1.83$ and $-1.53$ kcal/mol for conformation I at the AM1 level of approximation.

From Tables 2, 3, and 5, we see that the intra-helix hydrogen bond parameters obtained from AM1 and PM3 for conformation I are almost identical to each other, although PM3 predicts a slightly stronger intra-helix hydrogen bond energy than AM1. The intra-helix hydrogen bond energy we obtained from PM3 for conformation II is almost identical to that from PM3 for conformation I. These are the interactions that bond the helices together within each triple helix. However, clear differences are seen when we investigate the inter-helix interactions in these two conformations. These are the ones that stabilize the triple helices within the crystal.

The inter-helix hydrogen bond energy is much stronger for conformation II. In conformation I, the two different kinds of inter-helix hydrogen bonds are $O_W$-$H_{W1}$-$O_W$ and $O_W$-$H_{W2}$-$O(4)$. In conformation II, the two different kinds of inter-helix hydrogen bonds are $O_W$-$H_{W}$-$O(5)$ and $O_W$-$H_{W}$-$O(3)$. In addition, we also found four additional close contacts in conformation II between $C(2)$ and $O_W$, $C(3)$ and $O_W$, $C(4)$ and $O_W$, and $C(5)$ and $O(4)$, which all involve $C-$H-$\cdots$O-type weak hydrogen bond interactions. It is likely that these $C-$H-$\cdots$O-type weak hydrogen bonds are responsible for the much stronger inter-helix hydrogen bond energy found in conformation II. Since the difference of the inter-helix hydrogen bond energy between conformation II and conformation I in PM3 is approximately 8 kcal/mol, the average energy contribution from each of these four $C-$H-$\cdots$O weak hydrogen bonds is estimated to be approximately 2 kcal/mol, which is consistent with the typical $C-$H-$\cdots$O bond energy. 

Figure 5. Predicted projection of the unit cell in the ab plane for the triple helical solid of the hydrated (1→3)-β-D-xylan (conformation I) calculated at the AM1 level of approximation. Heavy dashed lines indicate the intra-helix hydrogen bonds, and thin dashed lines indicate the inter-helix hydrogen bonds. The hydrogen atoms on the xylose residues are omitted.

Figure 6. Predicted projection of the triple helical solid in the ac plane for the hydrated (1→3)-β-D-xylan (conformation I) calculated at the AM1 level of approximation. The fiber repeat of the helix is 1/3 of the molecular repeat, and the hydrogen atoms on the xylose residues are omitted.
From Tables 3 and 5, we see that the predicted O(2)···O(2) bond length in hydrated xylan is 2.9 Å from AM1 and 3.0 Å from PM3 for conformation I. These values are very similar to one another and to the corresponding data for glucan. The O(2)···O(2) bond length is 2.9 Å from PM3 for conformation II, but the O(2)--H···O(2) angle is only 94°. Since the optimal bond angle for O--H···O interactions should be closer to 180°, we expect that this interaction is substantially weakened.

Miyoshi et al. proposed two possibilities for the hydrogen bonds in the anhydrous (1→3)-β-D-xylan triple helix using cluster calculations with MOPAC and B3LYP approximations. Their inter-ring hydrogen bond length between O(4) and O(1) is 2.9 Å in their most stable conformation. The actual conformation in the anhydrous form for (1→3)-β-D-xylan would need to be verified experimentally.

From Table 4, we see that the cell dimensions for hydrated xylan calculated in conformation I agree excellently with those from the experimental data, with almost perfect agreement between AM1 and PM3 in the a and b dimensions. However, for conformation II, the a and b cell dimensions calculated at the PM3 level of approximation are significantly smaller than those from experiments. It is likely that the C--H···O type interactions occurring in conformation II and absent in conformation I are responsible for this.

4. CONCLUSIONS

In comparing the intra-helix hydrogen bond energies and parameters we obtained for glucan and for the hydrated xylan solids, we found that AM1 gave almost the same values for both the bond energies and bond parameters for these two polysaccharides. PM3 gave similar intra-helix hydrogen bond lengths for these two polysaccharides, but slightly different intra-helix hydrogen bond energies. Both methods predict stable intra-helix hydrogen bonds in these two polysaccharides.

In comparing the inter-helix hydrogen bond energies for these two polysaccharides, we found that there are clear differences in their bond energies. PM3 gave strong inter-helix bond energies for glucan and for conformation II in hydrated xylan, but predicted a very weak bond energy for conformation I in hydrated xylan. AM1 gave a moderately strong bond energy for glucan, but a weak bond energy for hydrated xylan in conformation I. We therefore conclude that the stronger inter-helix bond energies for glucan and for conformation II in hydrated xylan resulted from the interactions from both O--H···O and C--H···O hydrogen bonds, which contradicts the traditional interpretation that only the O--H···O hydrogen
shorter the existence of a second more stable conformation for hydrated xylan. Furthermore, the PM3 calculations predicted those from PM3 in all calculations. The cell dimensions lengths from AM1 were closer to the experimental values than C-H...O interactions. It is, of course, possible that these interactions to be weaker than the O-H...O interactions. However, we expect these interactions to be weaker than the C-H...O or C-H...O interactions. It is, of course, possible that these missing van der Waals interactions could be potentially important, but we cannot estimate their potential effect on stabilizing the structures discussed here.

We also found that the intra- and inter-helix hydrogen bond lengths from AM1 were closer to the experimental values than those from PM3 in all calculations. The cell dimensions calculated at both levels of approximation agreed excellently with the experimental values for glucan and conformation I of hydrated xylan. Furthermore, the PM3 calculations predicted the existence of a second more stable conformation for hydrated xylan, which was predicted to have considerably shorter a and b cell dimensions than found in the experimental structure.

In conclusion, the cyclic periodic wave function approach when combined with the AM1 and PM3 levels of approximation gives reliable results for solid-state systems, which are stabilized by strong hydrogen bonds.

### Table 5. Parameters of the Inter-Helix Hydrogen Bonds for the Hydrated 6/1-Triple Helical (1→3)-\(\beta\)-D-Xylan Solids

| hydrated xylan solid | \(d_{1}^{a}\) (Å) | \(\theta_{1}^{a}\) (°) | \(d_{2}^{b}\) (Å) | \(\theta_{2}^{b}\) (°) |
|----------------------|-----------------|-----------------|-----------------|-----------------|
| PM3 conformation I   | \(O_{w} \cdot H_{w} \cdot O_{w}\) | 2.7  | 146 | 3.3  | 111 |
| PM3 conformation II  | \(O_{w} \cdot O(5)\) | 3.1  | 143 | 3.9  | 147 |
| AM1 conformation I   | \(O_{w} \cdot O_{w}\) | 2.7  | 121 | 2.7  | 97  |
|                      | \(O_{w} \cdot O(4)\) | 2.7  | 146 |

*Different O...O bond distances for \(O_{w} \cdot H_{w} \cdot O_{w}\) hydrogen bonds. Different bond angles for \(O_{w} \cdot H_{w} \cdot O_{w}\) hydrogen bonds. Different bond angles for C-H...O hydrogen bonds. Different bond angles for C-H...O hydrogen bonds.*

### Table 6. Hydration Energies for 6/1-Triple Helices of Hydrated (1→3)-\(\beta\)-D-Xylans

|                         | \(\Delta H_{f}^{\text{total}}\) (kcal/mol) | \(\Delta H_{f}^{\text{th}
\text{t}}\) (kcal/mol) | \(\Delta H_{f}^{\text{int}}\) (kcal/mol) | \(\Delta H_{f}^{\text{pol}}\) (kcal/mol) |
|-------------------------|----------------------------------|------------------|----------------------------------|----------------------------------|
| AM1                     | 559.33                           | -751.24          | -14.22                           | -4.74                           |
| PM3                     | 500.75                           | -666.21          | -5.80                            | -1.93                           |

*Calculated heat of formation for the anhydrous triple helix. Calculated heat of formation for the corresponding hydrated triple helix. Total hydration energy of the corresponding triple helix. Net hydration energy per residue for the corresponding triple helix.*

Notes
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