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Investigation of the structure and interaction of cellulose triacetate I crystal using ab initio calculations

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ABSTRACT

The crystal structure of cellulose triacetate I (CTA I) was investigated using first-principles density functional theory (DFT) calculations. The results are in good agreement with the experimental structure obtained by Sikorski et al. when performing the calculation with inclusion of the dispersion correction. However, the cell parameters calculated with inclusion of the dispersion correction are slightly smaller than those experimentally obtained, especially along the *a*-axis. This smaller cell parameter could be reasonably explained by considering thermal expansion effects, since optimization with the density functional calculation gives the structure without inclusion of thermal effects. The atoms-in-molecules (AIM) theory is also employed to identify and characterize interatomic interactions in the CTA I crystal. CH/O interactions sites are shown to exist in the crystal structure of CTA I. Moreover, CH/O interactions are considered the main interactions in operation to maintain the crystal structure of CTA I.

1. Introduction

Cellulose triacetate (CTA) is one of the more common industrially manufactured cellulose derivatives in use for many years in the fiber and textile industries and currently used in a variety of commercial products such as films and fibers. The applications of CTA have seen significant expansion not only to these mass production fields, but also to high-technology fields. For example, CTA has been recognized as a powerful chiral polymeric sorbent for chromatographic separation of enantiomers, and its industrial application is widespread in chemical and pharmaceutical fields. As for its structure, CTA is known to adopt two main types of crystalline polymorphs, CTA I and CTA II, which are derived from the corresponding cellulose I and II, respectively.[1,2] According to Sprague et al.,[1] CTA I can only be obtained by heterogeneous acetylation of native cellulose I fibers. Numerous structural studies of CTA I have been conducted over the years; the crystal structure of CTA I has been investigated by X-ray diffraction, NMR and IR spectroscopic techniques, and computational theoretical calculation methods, and several unit cell models have been proposed.[3–5] Although the crystal structure of CTA I has been refined according to these models, its exact determination is still a matter of controversy. Recently, Sikorski et al.[6] proposed a further refined crystal structure of CTA I with cell dimensions of $a = 0.5939$ nm, $b = 1.1431$ nm, c (chain axis) = 1.046 nm, and $\gamma = 95.4$ from X-ray diffraction experiments using a highly oriented fiber sample of CTA I. This model was in good agreement with the observed X-ray diffraction intensities, with a crystallographic reliability index of $R = 0.224$. Moreover, cross polarization–magic angle spinning (CP/MAS) ^{13}C NMR spectroscopic studies demonstrated that each ring carbon atom of CTA I only shows a singlet resonance;[7,8] this indicates that the asymmetric unit of CTA I should be composed of only a single CTA chemical unit. The crystal structure determined by Sikorski et al.[6] can provide an explanation for these NMR results.

Recent reports have described crystal structure determinations of cellulose using ab initio quantum chemical calculations.[9,10] These reports indicated that the polymer crystal structure could be calculated with a reliable accuracy. In our previous report,[11] we applied a similar approach to investigate the crystal structures of CTA I using the coordinates obtained by Sikorski et al.[6] as an initial geometry. Sikorski et al.[6] used a molecular mechanics method to optimize their model with the condition of cell size fixed to the experimental value in the refinement process of their CTA I crystal structure. In our calculation, we performed a full optimization of the crystal structure, which included relaxation of the cell parameters using density functional theory (DFT) calculations; the results of our study showed that the ab initio calculation supports their crystal structure. Here, we present the full work for the optimization of the CTA I crystal structure. The effects of crystal thermal expansion are discussed in detail along with a comparison of the

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experimental data. The interactions involved in the formation of crystal structure of CTA I are also evaluated.

2. Computational details

A schematic illustration and the nomenclature of the CTA chain are shown in Figure 1. Initial parameters of the unit cell and the atomic coordinates of CTA I were used as determined by Sikorski et al.[6] The variable-cell relaxation (abbreviated later as vc-relax), which optimizes both the cell parameters and internal geometry optimization with monoclinic P1 space group, was performed with the Quantum ESPRESSO program package.[12] We used the ultra-soft pseudopotentials (US-PP) plane wave basis sets, which were downloaded from the Quantum ESPRESSO Homepage.[13] The convergences of energies and the structure were tested with different cutoff energy values of 50, 70, 100, and 150 Ry. Monkhorst–Pack *k*-point grids[14] were tested with 2 × 2 × 2, 3 × 3 × 3, and 4 × 4 × 4. The Perdew–Burke–Ernzerhof (PBE) gradient-corrected density functional[15] was used. The long-range van der Waals (vdW)-type correction term was included by using the DFT-D approach (PBE-D).[16]

NMR chemical shift calculations were performed using the GIPAW method[17] as a single-point calculation on both the crystal structure obtained experimentally by Sikorski et al. and the theoretically optimized structures using the PBE and PBE-D methods. After the test calculations with different *k*-point spacings and cutoff energies, a cutoff energy (E_{cut}) of 70 Ry and the 3 × 3 × 3 Monkhorst–Pack *k*-point grid was chosen for all chemical shift calculations. The GIPAW module is available in the Quantum ESPRESSO program package. Data visualization was done using VMD1.8.7.[18] Input files for atoms-in-molecules (AIM) analysis[19] were generated by Gaussian 09[20] and analyzed using the AIM 2000 package.[21] The wave functions generated from the quantum chemical calculations were calculated using the M062X/6-31+G(d,p) basis set and used in the AIM calculation. AIM analysis was used to calculate the electron density, ρ, and the Laplacian of the electron density, $\Delta\rho$, at the bond critical points.

3. Results and discussion

3.1. Optimized conformation of CTA I

Before discussing the crystal structure in detail, it would be important to check the convergence of optimized cell parameters according to the selection of the parameters in the calculation such as the functional, kinetic energy cutoff, *k*-points, etc. The optimized cell parameters calculated using different kinetic energy cutoff values with the PBE functional are shown in Table 1. As can be seen in Table 1, the cell parameters of *b*, *c*, and γ were very similar, even with variations in the E_{cut} value. However, cell parameter *a* calculated using E_{cut} = 50 Ry showed a slightly smaller value compared to others obtained with larger E_{cut} values. Above an E_{cut} value of 70 Ry, cell parameter *a* showed almost same value irrespective of the E_{cut} value increments, that is, this cell parameter can be considered to be converged at E_{cut} = 70 Ry for this crystal. A similar calculation was performed on the cell parameters with the PBE-D functional, the results of which are shown in Table 2. A similar dependence of the cell parameter on the E_{cut} value was observed. That is, cell parameters of *b*, *c*, and γ were similar to each other even if the E_{cut} value varied, and cell parameter *a* calculated using E_{cut} = 50 Ry showed a slightly larger value compared to others obtained with larger E_{cut} values. These results again suggest that E_{cut} = 70 Ry is a maximum economical choice for the calculation of cell parameters of this crystal.

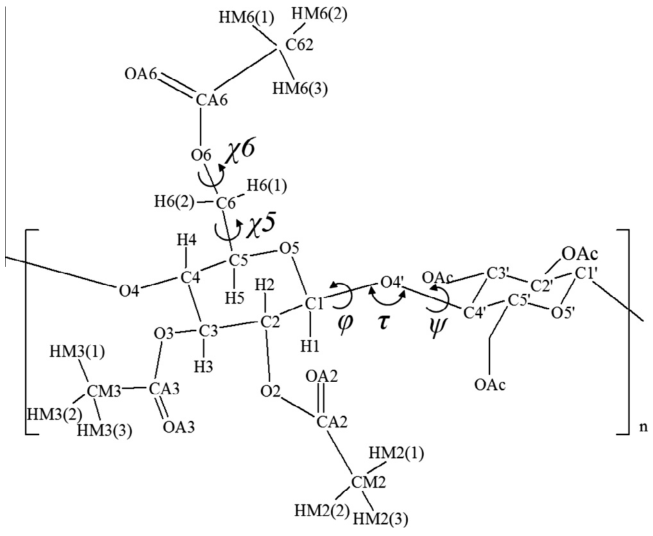

Figure 1. Nomenclature of cellulose triacetate.

The Monkhorst–Pack *k*-point grids[11] selected for testing were 2 × 2 × 2, 3 × 3 × 3, and 4 × 4 × 4. The results calculated using PBE and PBE-D functional with the E_{cut} value of 70 Ry are shown in Tables 3 and 4, respectively. All cell parameters (*a*, *b*, *c*, and γ) did not show any dependence on the Monkhorst–Pack *k*-point grids selected. As the model system used in this calculation is large, the selection of the *k*-point grid does not affect the calculation results. According to this result, the 2 × 2 × 2 Monkhorst–Pack *k*-point grid was used in subsequent crystal structure optimization.

Table 1
Optimized cell parameters of CTA I obtained from DFT calculations with PBE functional at several values of kinetic energy cutoff, E_{cut}

	E_{cut}/Ry			
	50	70	100	150
a (Å)	6.19	6.45	6.52	6.45
b (Å)	11.70	11.78	11.72	11.77
c (Å)	10.61	10.64	10.65	10.64
γ (°)	96.34	95.57	94.07	95.58

The values of *k*-points are 2 × 2 × 2.

Table 2
Optimized cell parameters of CTA I obtained from DFT calculations with PBE-D functional at several values of kinetic energy cutoff, E_{cut}

	E_{cut}/Ry			
	50	70	100	150
a (Å)	5.65	5.61	5.60	5.61
b (Å)	11.44	11.42	11.40	11.40
c (Å)	10.53	10.55	11.55	10.55
γ (°)	93.45	94.77	94.77	94.79

The values of *k*-points are 2 × 2 × 2.

Table 3
Optimized cell parameters of CTA I obtained from DFT calculations with PBE functional at several *k*-points with kinetic energy cutoff, E_{cut} = 70 Ry

	k-Points		
	2 × 2 × 2	3 × 3 × 3	4 × 4 × 4
a (Å)	6.45	6.44	6.40
b (Å)	11.78	11.77	11.77
c (Å)	10.64	10.63	10.63
γ (°)	95.57	95.52	95.52