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Accelerated tight-binding calculation study on the deprotonation of the monofucosyllacto-N-hexaose I (MFLNH I)

○Xiaolei Wang, Kazumi Serizawa, Ai Suzuki, Hideyuki Tsuboi, Nozomu Hatakeyama, Akira Endou, Hiromitsu Takaba, Momoji Kubo, Akira Miyamoto
Department of Chemical Engineering, Tohoku University.
xiaolei@aki.che.tohoku.ac.jp.

【Introduction】

Tandems Mass spectrometry (MS^n) investigation in the negative-ion mode yields unambiguous structural information for oligosaccharides. In the current work, we attempt to investigate the strengths of the bond in MFLNH I to deduce the positions of deprotonation. As precursor, the deprotonated molecule was used for further study of the fragmentation of oligosaccharides. Accelerated tight-binding calculation method is an effective tool to know the bond strengths in monofucosyllacto-N-hexaose I (MFLNH I) which have been well investigated by MS [1]. We used this method to know the acidity of hydroxyl group in this molecule. The more acidity of hydroxyl group, the more possibility the deprotonation take place.

【Method】

Accelerated tight-binding calculation method, which is 10 million times faster than conventional first principles method, was used in our calculation. Tight-binding calculation method was applied to investigate the molecule in the form of "New-Colors". In the "New-Colors" program, high efficiency of computation is realized by adopting parameters in the Hamiltonian. In our program, the parameters are determined on the basis of density functional theory calculation results. This can realize both high calculation speed and high accuracy [2,3,4]. Total energy of a system is obtained by using the following equation.

$$E = \sum_{k=1}^{occ} n_k \varepsilon_k + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{Z_i Z_j e^2}{r_{ij}} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} E_{ij}^{repul}\left(r_{ij}\right)$$

where the first, second, and third terms on the right-hand side refer to the molecular orbital (MO) energy, columbic energy, and exchange-repulsion energy, respectively.

【Results and Discussion】

Fig. 1 shows the structure of MFLNH- I molecule labeled with pyrene butanoic acid hydrazine (PHB).

According to the systematic nomenclature of carbohydrates, the carbon atoms of monosaccharide are numbered consecutively in such a way that has shown in the Fig.2. There are many hydroxyl groups in this molecule. To sort that out, we described the O-H bond in hydroxyl groups in the following way: chain number+saccharide+carbon atom number which has shown in the table 1.

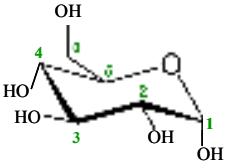
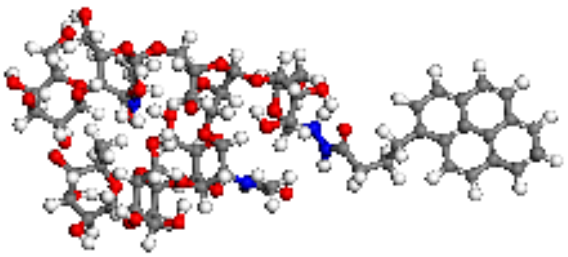


Fig.2 Numbering of carbon atom in monosaccharide

Table 1 shows the bond population (BP) and bond energies (BE) of partial hydroxyl group from colors calculation on MDLNH-I molecule. This shows that these hydroxyl groups in MDLNH-I molecule display different acidity and help us to know where in this molecule the deprotonation take place.



a chain
Gal β 1-O-4GlcNAc β 1-O-6
Gal β 1-O-4Glc-PBH
Fuc α 1-O-2Gal β 1-O3GlcNAc β 1-O3
b chain

Figure 1 Composition of oligosaccharide (MFLNH- Ⅰ) which is labeled with PHB

Table 1 Bond population (BP) and bond energies (BE) of 5 weakest bonds

Bond	BP	BE (kcal/mol)
b-GlcNac O-H (6)	0.62	-111.51
a-Glc O-H (6)	0.64	-112.67
b-Gal O-H (2)	0.63	-112.88
Glc O-H (3)	0.63	-113.61
Glc O-H (2)	0.64	-114.81

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