

^{13}C NMR 分光法, 赤外分光法および理論計算によるアミノ酸誘導体の溶液中での分子間および分子内相互作用の評価

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^{13}C NMR and IR Spectroscopic and Computational Studies of Intra- and Intermolecular Interactions of Amino Acid Derivatives in Solutions (¹Graduate School of Science and Technology, Hiroshima Institute of Technology, ²Graduate School of Technology, Muroran Institute of Technology) ○Yoshikazu HIRAGA,¹ Satomi NIWAYAMA,² Ryosuke HOSHIDE²

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Carbonyl compounds are known to form aggregates by intermolecular forces, such as hydrogen bonding and dipole-dipole interaction, etc. in a solution. In this study, ^{13}C NMR chemical shifts were monitored for evaluation of the interaction between amino acid derivatives and various solvents with different polarities.

Figures 1(a) and 1(b) show behaviors of ^{13}C NMR chemical shifts of the carbonyl carbons of the carboxyl groups and those of the Boc groups in *N*-Boc-proline-alanine methyl ester **1a** and *N*-Boc-proline-serine methyl ester **1b**, respectively, in various solvents. As shown in Fig. 1(a) and 1(b), with increase of the solvent polarity, the ^{13}C NMR chemical shifts of the carbonyl group in **1a** (■, ▲) and **1b** (■) moved downfield, while those of the carbomethoxy group in **1b** (▲) were almost constant. On the other hand, the behaviors of the chemical shifts of the carbonyl carbon in the Boc group of **1a** (●) and **1b** (●) showed a similar tendency and were almost constant regardless of the solvent polarity.

To understand the behavior of the ^{13}C NMR chemical shifts of carbonyl carbons in **1a** and **1b**, the DFT calculations (B3LYP/6-31+G(d) level) were carried out. The most stable structures of **1a** and **1b** are shown in Fig. 1. In the most stable structure of **1a**, it was shown that intramolecular hydrogen bonding was formed between the oxygen atom of the carbonyl group (●) of Boc group and the hydrogen atom in the amide bond. Also, the carbonyl group (●) of the Boc group in **1b** formed intramolecular hydrogen bonding with the hydrogen atom of the amide bond, and the hydrogen atom of hydroxyl group of serine was close to the oxygen atom of the carbonyl carbon (■). These models supported the behaviors of the ^{13}C NMR chemical shifts of the carbonyl carbon in **1a** and **1b**. The behaviors of other amino acid derivatives in various polar solvents are under investigation.

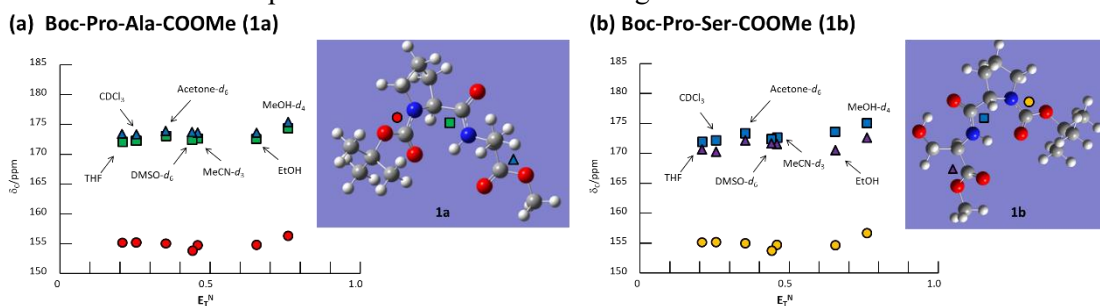


Fig 1. ^{13}C NMR chemical shifts of the carbonyl carbons in **1a** and **1b** and their most stable structures