

Development of quantitative evaluation for Through Space/Bond interactions and its application to the analysis of reactions and functional properties

江, 麗芝

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氏 名：江 麗芝

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(スルースペース／ボンド相互作用に対する定量的評価法の開発と反応・機能解析への応用)

区 分：甲

論 文 内 容 の 要 旨

In this thesis, I developed the through space/through bond (TS/TB) orbital interaction analysis method combined with polarizable continuum model (PCM) based on natural bond orbital (NBO) basis set (TS/TB-PCM method), making it available to analyze systems in solvent with large basis set. Then, I applied this method to analyze the mechanism of S_N2 reactions, and tested it for analyzing the large conducting materials with good nonlinear optical (NLO) performance.

First, we applied the TS/TB orbital interaction analysis to investigate the stereoelectronic effects on stabilizing the transition states (T-S(s)) of Menshutkin-type S_N2 reactions. The geometrical structures and Mulliken charge distributions have been compared to elucidate the substituent effects for the S_N2 reaction center. It is found that the substituents lower the activation energies by strengthening the orbital interactions in the S_N2 reaction process. When the electron-donating and electron-accepting substituents ($-C_6H_5$ and $-CHO$) are introduced to the same central carbon at the reaction center, the symmetry allows the $\pi-\pi^*$ interactions among the donor and acceptor in the T-S. It stabilizes the T-S much more than the reactant complex. When the $\sigma-\pi^*$ and $\pi-\sigma^*$ interactions are deleted from the system, the activation energy increases and turns close to the values of the systems which are without such substituents. It can be concluded that the $\pi-\pi^*$, $\sigma-\pi^*$, and $\pi-\sigma^*$ interactions cooperatively accelerate the S_N2 reaction by stabilizing its T-S.

The solvent effects are significant in the reactions. We developed a method to theoretically interpret the mechanism of acceleration for Menshutkin-type reactions in solutions, from the orbital interaction view, utilizing the TS/TB interaction analysis in the polarizable continuum model (PCM). Different method levels were tested to determine the substituent effects on the reactions of NH_3 attacking para-substituted benzyl bromide. The results of the Mulliken charge analysis showed that the para-substituted benzyl group ($-C_6H_4Y$) received negative charges through

the reaction process, and both electron-donating and electron-withdrawing substituents Y forced $-\text{C}_6\text{H}_4\text{Y}$ groups to receive greater charges. The TS/TB orbital interaction analysis results revealed that the key orbital interactions for stabilizing the T-S(s) of the systems with substituents $\text{Y} = \text{NH}_2$ and $\text{Y} = \text{NO}_2$ in water were $\text{n}(\text{NH}_2)-\pi^*(\text{ph})$ (ph = phenyl) and $\pi(\text{ph})-\pi^*(\text{NO}_2)$ interactions, respectively. Stronger interactions between $\pi^*(\text{ph})$ and $\sigma^*(\text{C}_\alpha\text{-Br})$ occurred because of the $\text{n}(\text{NH}_2)-\pi^*(\text{ph})$ and $\pi(\text{ph})-\pi^*(\text{NO}_2)$ interactions that resulted when para-substituents $-\text{NH}_2$ and $-\text{NO}_2$, respectively, were added to the system. These stronger $\pi^*(\text{ph})-\sigma^*(\text{C}_\alpha\text{-Br})$ interactions stabilized the T-S and enabled the Br leaving group to leave more easily.

Besides the organic reactions mentioned above, we also focused on the functional properties of oligomers/polymers because the TS/TB interaction analysis must be useful to get insights into the relationship between functional properties and electronic states in large systems. Among functional properties, we first adopted conducting and nonlinear optical properties (NLO) in oligomers related to structural transition. The NLO properties are sensitive to the geometrical structures, and are strongly related to the electron transfer. The TS/TB interaction analysis was applied to analyze the structural transformations of isonaphthothiophene $(\text{INT})_n$ oligomers, because we found an interesting phenomenon that as the chain length n increased, the geometrical conformations of $(\text{INT})_n$ changed and then the energy gap suddenly decreased. The conducting properties of $(\text{INT})_n$ were examined by the density of states (DOS) and local DOS analyses. The energy potentials and dihedral angle rotation effect were explored to determine the most preferred stable structures. The geometrical and intrinsic charge characters were analyzed by UV/vis/NIR spectra and confirmed by frontier orbital analysis. Interestingly, the (hyper)polarizabilities of $(\text{INT})_n$ oligomers increased sharply as the chain length increased. Additionally, the importance of the side β double bonds effect on the structural transformation was also detected by a new quantum chemical technique resulting in a potential polymer conductor that can be controlled by modifying its side chains.

One of the advantages of the developed TS/TB orbital interaction analysis method is its quantitative evaluation of the orbital interactions. By comparing the interactions, the important part can be estimated. Furthermore, the orbital interactions in solvents can be estimated by our TS/TB-PCM method. We aim to develop this method for large systems at high levels. The improvement of the efficiency of the method for large systems could be a further work.