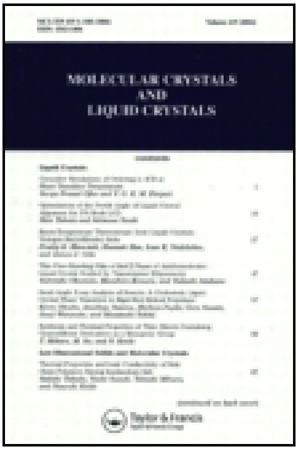

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Designing Molecular Tweezers Aimed at Molecular Recognition

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Designing Molecular Tweezers Aimed at Molecular Recognition

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We have designed and synthesized a schiff base ligand, N,N′-bis(o-hydroxybenzylidene)diethylenetriamine, as a host that exhibits the strong binding ability to salicylaldehyde as a guest. The binding characteristics of the interaction between the schiff base and salicylaldehyde have been obtained by NMR spectroscopy study. The reversible binding mechanism depending upon the solution pH has been monitored by NMR spectroscopy during the acid titration reaction. The interaction between the schiff base and salicylaldehyde was also confirmed by COSY and NOE experiments.

Keywords: schiff base; molecular tweezers; molecular recognition; host; guest

INTRODUCTION

Recently, noncovalent interactions between two different molecules have attracted attentions and become an important subject in the fields of science covering chemical, physical and biological features.[1]-[8] In particular, the selective binding via the noncovalent interaction such as hydrogen bonding is the basis of the main concept in molecular recognition studies.[5]-[15] We have been designing and synthesizing molecular tweezers assembly aimed at molecular recognition in the 1:1 complex between a schiff base and salicylaldehyde. In this system, it is confirmed that the schiff base molecule, N,N'-bis(o-hydroxybenzylidene)diethylenetriamine (FIGURE 1-b) can capture a salicylaldehyde molecule.

EXPERIMENTAL

The schiff base compound (FIGURE 1-b) was obtaineded by the reaction of salicylaldehyde (2 moles) and diethylenetriamine (1 mole) in acetonitrile. In this reaction, the 1:1 complex between a schiff base and salicylaldehyde (FIGURE 1-c) has been obtained. The pure schiff base product and the 1:1 complex were successfully separated by the column chromatography. The 1:1 complex was also prepared by the reaction of the same equivalents of schiff base and salicylaldehyde, respectively and purified by the column chromatography. All the ^{1}H-NMR experiments were performed with FT-300MHz Bruker Aspect 3000 spectrometer.

RESULTS AND DISCUSSION

Here we report that the designed schiff base exhibits a strong binding capability to a salicylaldehyde molecule, one of starting materials in the reaction (FIGURE 1). During the purification of the schiff base compound by column chromatography, two compounds were acquired. From ^{1}H-NMR spectra, it is confirmed that one is the pure schiff base and the other is the 1:1 complex of the schiff base and salicylaldehyde. This complex has been characterized systematically by ^{1}H-NMR spectroscopy. It is certain that the driving forces for the complex formation of the schiff base and salicylaldehyde are the hydrogen bonding and π-π stacking interaction between aromatic planes.[15] FIGURE 1 shows the schematic diagram of the formation of the complex. FIGURE 2 (a) is the typical ^{1}H-NMR spectrum of the pure schiff base as shown in FIGURE 1 (b). The spectrum (b) corresponds to the pure salicylaldehyde. ^{1}H-NMR titration of the schiff base with salicylaldehyde has been performed and the binding characteristics have been monitored [FIGURE 2 (c~g)]. Each spectrum in Figure 2 (c)~(g)

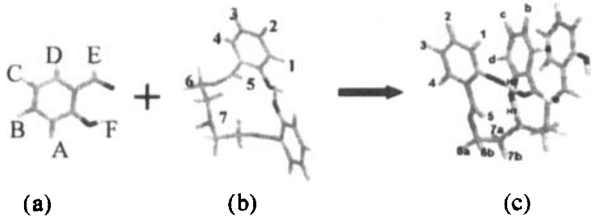

FIGURE 1 The complex formation of schiff base with salicylaldehyde
(a) Salicylaldehyde, (b) N,N'-bis(o-hydroxybenzylidene)diethylenetriamine
(c) Schiff base - salicylaldehyde complex

indicates that the addition of every 0.2 equivalents of salicylaldehyde to the schiff base exhibits the gradual complex formation based on the noncovalent intermolecular interaction such as hydrogen bonding (FIGURE 1-c).

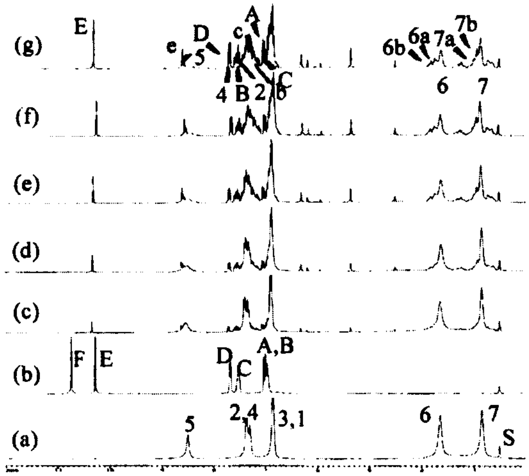

FIGURE 2 NMR Titration of the schiff base (in DMSO-d_6) with varying amounts of salicylaldehyde. (a) Schiff base, (b) Salicylaldehyde, (c)-(g) Titration spectra obtained after adding every 0.2 equivalents of salicylaldehyde to the schiff base solution. Spectral peaks are assigned to the corresponding protons shown in FIGURE1.

With the complex forming, the intramolecular hydrogen bonding gets weaker between a CO group and an OH group within the salicylaldehyde (peak "F" in FIGURE 2-b), while the intermolecular hydrogen bonding gets stronger between OH group of salicylaldehyde and NH of the schiff base, and between salicylaldehyde CO and OH group of the schiff base. These characteristics have been confirmed by the COSY experiments. The complex formation by intermolecular hydrogen bonding can be investigated by the NOE experiments.[4] When the intermolecular hydrogen bond (H_1) get irradiated, nearby H_2 hydrogen bond and a neighbor proton (a) exhibit positive NOEs (FIGURE 3-a). When the hydrogen bond H_2 get irradiated, 4 and 7a neighboring protons and the hydrogen bond H_1 show positive NOEs (FIGURE 3-b).

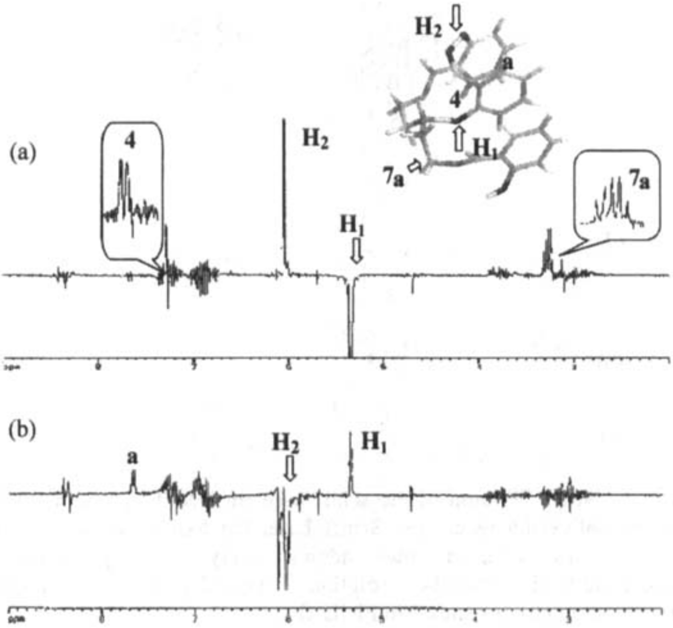

FIGURE 3 Intermolecular NOE spectra after irradiation of (a) H_1 and (b) H_2 protons.

Similarly when the imine proton gets irradiated, nearby 6, 4 and b protons exhibit positive NOEs. During the acid titration reaction the reversible binding mechanism depending upon the solution pH has been monitored by NMR spectroscopy. From these data, it is sure that the designed schiff base possesses potential capability of noncovalent intermolecular interactions for the basis of the molecular recognition.

CONCLUSION

We have designed and synthesized a new schiff base molecule, N,N'-bis(o-hydroxybenzylidene)diethylenetriamine, which exhibits the noncovalent intermolecular interaction to salicylaldehyde. The binding mechanism has been characterized by NMR spectroscopy. The interaction between a schiff base and salicylaldehyde was also confirmed by COSY and NOE experiments. The 1:1 complex exhibits reversible binding mechanism depending upon the solution pH. Future papers will describe more detailed properties in these systems.

Acknowledgements

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