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Molecular Recognition: Schiff Base as Molecular Tweezers

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The self-assembling via hydrogen bonding can be the important basis of the main concept in molecular recognition. We have designed and modified the organic schiff base, N,N'-bis(o-hydroxybenzylidene)diethylenetriamine and its halo- (Cl- or Br-) derivatives as artificial receptors that exhibit the strong binding characteristics to barbituric acid as a guest. ^{1}H-NMR spectroscopic titration has been performed to characterize the noncovalent intermolecular interaction between the schiff base or its halo-derivatives and a barbituric acid molecule.

Keywords: H-bonding; molecular tweezers; molecular recognition; receptor; guest; self-assembly

INTRODUCTION

Molecular recognition due to noncovalent intermolecular interactions such as hydrogen bonding has become an important subject in areas of chemistry, biology and physiology.[1]-[6] The hydrogen bonds between the receptor and the neutral molecule have been known as the basis of the main concept in molecular recognition studies.[5]-[9] We have designed and modified the organic schiff base receptor molecules that exhibit the strong binding ability to a barbituric acid as a guest. In this study, it is confirmed that according to ^{1}H-NMR spectroscopy the schiff base, N,N'-bis(o-hydroxybenzylidene) diethylenetriamine and its halo- (Cl- or Br-) derivatives can capture a barbituric acid molecule to form the stable complex via hydrogen bonding.

EXPERIMENTAL

The schiff base and its halo-derivative compounds were prepared by the reaction of two moles of salicylaldehyde or its halo- (Cl- or Br-) derivatives and one mole of diethylenetriamine in methanol at 65°C for 1 hour. The schiff base (FIGURE 1-**I**) or its halo-derivatives can be purified by the column chromatography from the reaction mixture. The 1:1 complex can be prepared by the reaction of the equimolar amount of schiff base and barbituric acid, respectively. All the ^{1}H-NMR experiments were performed with FT-300MHz Bruker Aspect 3000 spectrometer.

RESULTS AND DISCUSSION

We have prepared the synthetic receptors such as schiff base and its derivative molecules for a neutral molecule. Surprisingly it has been proven that the molecules exhibit the strong binding ability to the barbituric acid (FIGURE 1). ^{1}H-NMR spectroscopy has been performed to characterize the features of the interaction between the schiff base and a barbituric acid. It is important that the driving force for the complex formation of the schiff base with barbituric acid is the noncovalent hydrogen bonding interaction. FIGURE 1 shows that a schematic diagram of the formation of the complex.

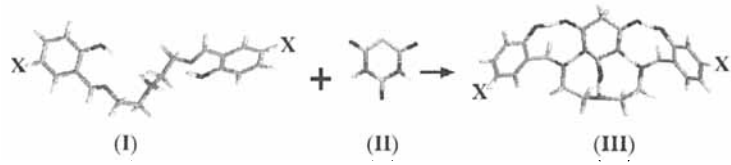

FIGURE 1 The complex formation of the schiff base with barbituric acid
(I) N,N'-bis(o-hydroxybenzylidene)diethylenetriamine, where X = H, Cl or Br, **(II)** Barbituric acid, and **(III)** Schiff base - Barbituric acid complex

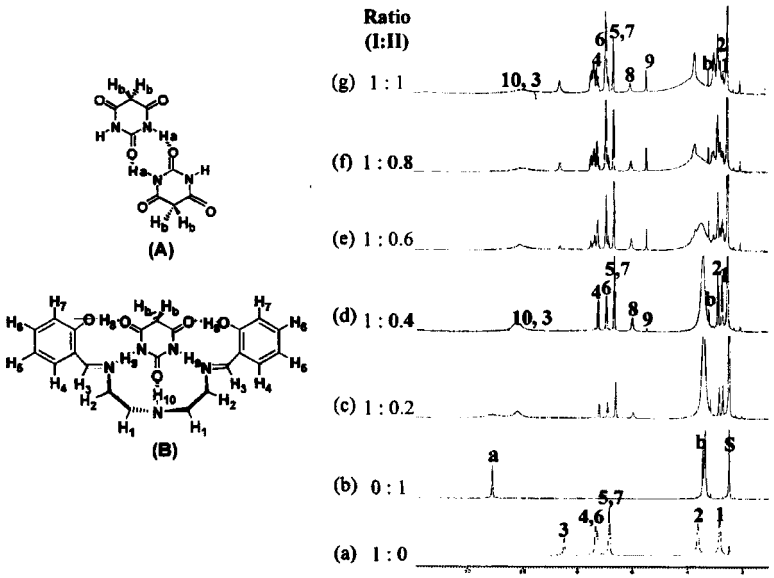

FIGURE 2 (a) ^{1}H-NMR spectrum corresponds to the pure schiff base (**I**), where X is H_5. (b) The spectrum shows an intermolecular hydrogen bond, **Ha**, between two barbituric acid molecules, **(A)**. Peak S is from the DMSO-d_6 solvent. (c) ~ (g) Spectroscopic titration of barbituric acid (**II**) with the schiff base (**I**) in DMSO-d_6.

^{1}H-NMR spectroscopic titration of barbituric acid (**II**) has been performed with the schiff base (**I**) and their binding characteristics have been monitored (FIGURE 2). With the addition of each 0.2 molar schiff base to barbituric acid, the intermolecular hydrogen bond, **Ha** in spectrum (a), between two barbituric acid molecules as in **(A)** is getting weaker and finally disappeared. At the same time intermolecular hydrogen bonds, $\mathbf{H_8}$, $\mathbf{H_9}$ and $\mathbf{H_{10}}$ as in **(B)**, between **(I)** and **(II)** get forming as indicated in spectra (c) ~ (g). Based on ^{1}H-NMR spectroscopic titration experiments, other halo-schiff bases (X = Cl and Br) also provide the similar interaction with barbituric acid with different stability. The formation constant (logKa) of the schiff base (X = H) with

barbituric acid is 3.87, while logKa's for halo-derivatives are 2.13 (X = Br) and 1.35 (X = Cl). According to the stability constants the complex formation is strongly dependent on the electronegativity of the substituent (X).

CONCLUSION

We have prepared a series of schiff base, N,N'-bis(o-hydroxybenzylidene) diethylenetriamine, and its halo-derivatives which exhibit the strong noncovalent interaction to barbituric acid. The interaction between the schiff base and barbituric acid was confirmed by ^{1}H-NMR spectroscopy. The stability of the complex depends strongly on the electronegativity of the substituent (X). Further studies are being carried out to elucidate detailed properties in these systems.

Acknowledgements

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