



Theoretical design and simulation of supramolecular polymer unit based on multiple hydrogen bonds



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ABSTRACT

The heterocyclic urea of deazapterin (**DeAP a**) and its protomeric conformers (**b**, **c**) with different substituents are selected as the building block for a series of dimers in different configurations. The stabilities of all dimers in various conditions have been investigated by density functional theory. Homodimer of **b** has more stability than other dimers. Topological analyses certify the coexistence of intermolecular with intramolecular H-bonds. Investigations into frequency demonstrate that all H-bonds show an evident red shift in their stretching vibrational frequencies. Electron donating substituents can provide favorable free energies of the dimer. Solvent effect computations suggest that the dimerization can be favored in weakly polar solvents, such as toluene and chloroform. UV–visible spectra exhibit obvious difference of maximum absorption wavelengths between monomers and dimers, thus may have potential applications for identifying intermolecular H-bonds and calculating association constant of **DeAP** equilibrium systems in experiments.

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1. Introduction

Recently, considerable progress has been achieved on design of novel supramolecular materials based on multi-point hydrogen-bonding motifs [1–11]. Owing to its directionality and strength, the hydrogen bond has become an ideal candidate for the noncovalent assembly of supramolecular and biological macromolecular (e.g., nucleic acids and proteins) building blocks [12–15]. Recent years, many researchers dedicated to designing and synthesizing molecules based on hydrogen-bonded modules with donor (D) and acceptor (A) functionalities [16]. By introducing more donor and acceptor sites into arrays, the strength of hydrogen bonds in polymers can be improved and then the selectivity are enhanced between two arrays. Once the hydrogen-bonded motifs interact, they can aggregate via two patterns: homodimers, when two equal units integrate in the way that the arrangement of the interacting functionalities (D or A) is self-complementary; heterodimers,

when two different units integrate in a complementary way of their functionalities.

Among the reversible and directional multiple hydrogen bonds, quadruple hydrogen-bonding arrays have been successfully applied in generating supramolecular polymers. In the past several decades, the self-complementary ureidopyrimidone [17–19] and ureidodeazapterin [20–24] units are the most successful in extensive research areas (notably in producing supramolecular polymers) for their strong affinity and synthetic accessibility. Heterocyclic urea of **DeAP a** (and its protomeric conformer **b**) (Fig. 1) containing self-complementary AADD hydrogen-bonding sites, was developed by Zimmerman's group [20a] without consideration of its protomeric form. It can generate exceedingly strong quadruple hydrogen-bonding hetero- and homodimers ($K_{\text{dim}} > 10^7 \text{ M}^{-1}$ in chloroform, among the largest association constant reported to date for neutral, hydrogen-bonding materials) with similar spatial arrangement of alkyl substituents, which is significant for applications in self-assembly. **DeAP a**, soluble in non-polar organic solvents, can be obtained conveniently by heating 2-amino-3H-pyrido-(2,3-d)pyrimidin-4-one, which is available in a two-step synthesis from commercially available 2,4-diamino-6-hydroxypyrimidine [25], and butylisocyanate. As shown in Fig. 1, **DeAP a** has four different tautomers in solution, which can dimerize to homo- or heterodimeric AADD–DDAA or DADA–ADAD arrays

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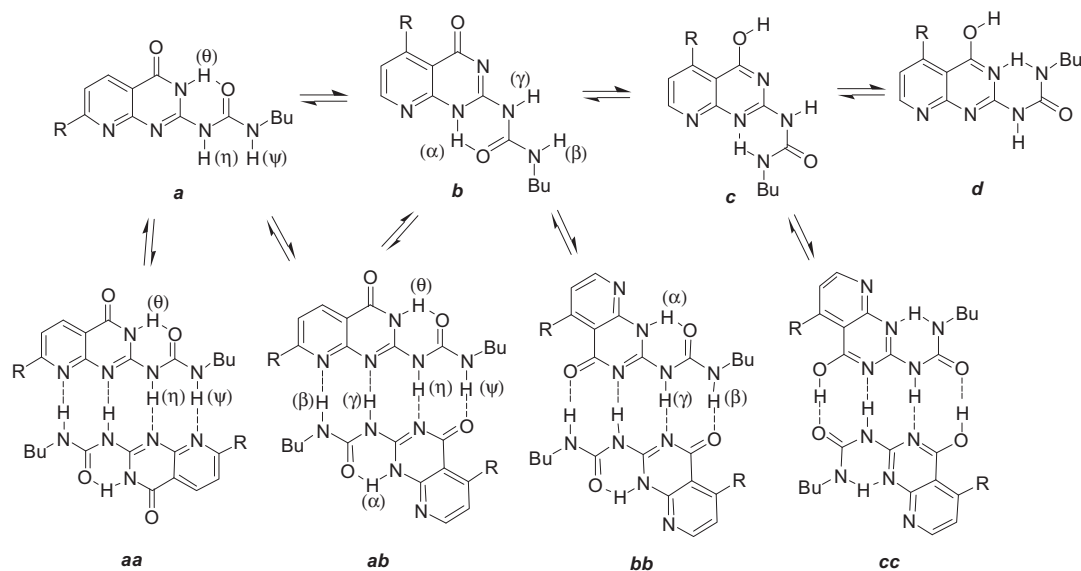


Fig. 1. Conformational, protomeric, and self-association equilibria of module **a**.

via quadruple hydrogen-bondings, except for **d**, a minor form which cannot form quadruple hydrogen bonded dimeric structure.

The synthetic accessibility of **DeAP a** and **b**, and the exceedingly strong H-bonds in corresponding complexes, make them promising modules for the construction of supramolecular oligomers and polymers. Although there is remarkable progress in the experimental aspect, few systematic theoretical studies have been reported [26], especially about the effect of solvent and substitution groups adjacent to the hydrogen bonds on the stability of dimers. Since electron donating substituents generally favor binding energies and free energies of dimerization, we introduced four hydrophobic and electron donating groups ($R = \text{methyl, propyl, } n\text{-butyl and iso-butyl}$) into the adjacent position of the quadruple hydrogen bonds, in the aim to protect the quadruple hydrogen bonds from damaging by the solvent molecules and further achieve more stable dimers.

In order to better understand the nature of hydrogen bonds theoretically, we will discuss the interactions of a series of dimers in different configurations (**aa**, **ab**, **bb**, **cc**) based on **DeAP a** and its protomeric conformers, involving interaction energies, interactions between accepting and donating orbitals of H-bonds and electronic properties of dimers. In addition, we will also report the effect of substitution groups adjacent to the hydrogen bonds and solvents on the stability of dimers.

2. Computational details

The density functional theory (DFT) has emerged during the past decades as a powerful methodology for the simulation of chemical systems. Despite taking less comprehensive electron correlations into consideration than the Second-order Moller-Plesset perturbation theory (MP2) method, DFT methods have been proved to characterize weak interactions sufficiently [26c,e,d,–28]. PBE1PBE [29–33], the hybridized function of GGA type, performed very well when dealing with hydrogen bonds energy in complexes. To test the applicability of the PBE1PBE functional in this research, we also considered alternative functional for the optimization calculations. Five functionals including PBE1PBE, X3LYP [34], M06-2X [35], ω B97XD [36] and B3LYP [37] were used to optimize the structure of DDAA–AADD hydrogen-bonded **UPy** dimer, which was widely used and available for experimental geometric parameters from Meijer's group [17b], with the same 6-31+G(d,p) basis

set (Table S1 (Supporting Information) and Scheme S1). It showed that geometric parameters from PBE1PBE and ω B97XD fitted much better with experimental data than other functional. Although ω B97XD actually gives more accurate results than PBE1PBE, the latter may perform faster and can be compared to previous studies more easily. Therefore, the PBE1PBE method was used to perform the geometry optimizations. All the calculations have been done with Gaussian09 [38] program, unless specified otherwise. To find proper basis set for systems investigated here, we conducted comparison analysis between the PBE1PBE/6-31G(d) geometry of the unsubstituted dimers ($R = \text{H}$) and those derived from higher level PBE1PBE/6-31+G(d,p) for available structures. It showed that PBE1PBE/6-31G(d) optimization can provide credible results with the insignificant geometry differences between the two computational levels which were less than 1.38% (Fig. S1). Geometry optimizations of monomers and dimers were carried out at the PBE1PBE/6-31G(d) level taking into account the balance between the computational economy and the accuracy. Frequency calculations were performed on all optimized geometries at the same level to verify the nature of all stationary points as minima. Based on the optimized configuration, we used the PBE1PBE/6-311++G(2df,2p) level for the single point energy calculations and the NPA analysis. The predictions of NMR and UV/visible absorption spectrum were calculated at the same level.

The effect of solvent was considered for geometric optimization and single point energy calculations, using polarizable continuum models (PCM) [39,40]. In the calculation of weak interactions such as multiple hydrogen bonding systems studied here, basis set superposition error (BSSE) would take up a considerable proportion and even lead to errors. Therefore, BSSE correction was calculated herein for all computations by the counterpoise (CP) method [41,42] of Boys and Bernardi based on the optimized structures. Since the CP method is incompatible with the PCM model, BSSE calculations for dimers in various solvents were conducted without applying the PCM model. To estimate the strength of hydrogen bonds, we calculated the binding energy with BSSE and zero-point energy (ZPE) corrections. To get a further understanding of hydrogen bonds in this work, the topological properties of electron densities for the monomers and complexes were computed at the PBE1PBE/6-311++G(2df,2p) level by combining Gaussian09 with Multiwfn3.3 [43–45] program.

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