7-Deazaguanine Analogues as Useful Modules for Quadruply Hydrogen-Bonded Heterocomplexation with Diamidonaphthyridine

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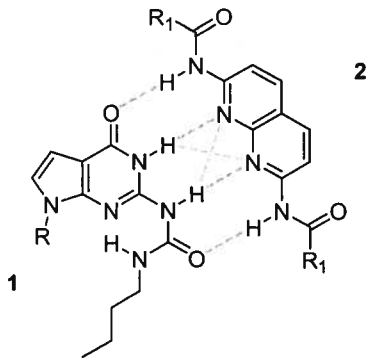
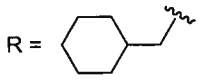
The quadruply hydrogen-bonded species represents an attractive class of complexes due to their high binding strengths in organic solvents and synthetic accessibility, giving it high application potential in supramolecular polymer chemistry. We have previously reported a ureidoguanosine analogue (UG) that was demonstrated to form a very stable complex with 2,7-diamido-1,8-naphthyridine (DAN, **2**) in $CHCl_3$ (K_{assoc} = 3 × 10^8 M^{-1}) (Park, T.; Nakashima, S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2005**, *127*(18), 6520-6521). Unlike other quadruply hydrogen-bonding species, which dimerize very strongly in $CHCl_3$ due to the availability of other tautomeric forms, UG did not exhibit any strong dimers. Thus, the fixed tautomer of UG allows for exceptional fidelity in its binding with **2**. UG was found to weakly oligomerize via the hydrogen acceptor sites on the Hoogsteen side ($K_{assoc} \approx$ 200 M^{-1}).

The 7-deazaguanine analogues **1** (DeUG) represent our latest efforts to develop ADDA hydrogen-bonding modules with even greater fidelity than UG by further minimizing self-association. Herein, we report the preparation of DeUG with N7 replaced by CH in an effort to abolish the oligomerization exhibited by UG. Our density functional theory (DFT) calculations, and previous studies on 7-deazaguanine in chloroform, suggest that its tautomeric behavior is similar to that of guanine, making 7-deazaguanine an ideal candidate for module construction. A lower limit of $K_{assoc} > 10^7$ M^{-1} in $CDCl_3$ for the heterocomplex with **2** was determined by NMR dilution experiments. Instead of the oligomerization exhibited by UG, DeUG was found to dimerize at K_{dim} = 840 M^{-1} in $CDCl_3$. The conformation of the ureido group of **1** and its fidelity with **2** are investigated as well.





$R_1 = C_6H_{13}$