Understanding cooperativity in hydrogen bonds of guanine quartets.

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We show that the cooperative reinforcement between hydrogen bonds in guanine quartets is not caused by resonance-assisted hydrogen bonding (RAHB). This follows from extensive computational analyses of guanine quartets (G4) and xanthine quartets (X4) based on dispersion-corrected density functional theory (DFT-D). Our investigations cover the situation of quartets in the gas phase, in aqueous solution as well as in telomere-like stacks. A new mechanism for cooperativity between hydrogen bonds in guanine quartets emerges from our quantitative Kohn-Sham molecular orbital (MO) and corresponding energy decomposition analyses (EDA). Our analyses reveal that the intriguing cooperativity originates from the charge separation that goes with donor–acceptor orbital interactions in the σ-electron system, and not from the strengthening caused by resonance in the π-electron system. The cooperativity mechanism proposed here is argued to apply, beyond the present model systems, also to other hydrogen bonds showing cooperativity effects.

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