

# Covalency in Hydrogen Bonds Causes Cooperativity in 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 ( $G_4$ ) and xanthine quartets ( $X_4$ ) 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 telomer-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  $\sigma$ -electron system, and not from the strengthening caused by resonance in the  $\pi$ -electron system. The cooperativity mechanism proposed here is argued to apply, beyond the present model systems, also to other hydrogen bonds showing cooperativity effects. Our finding is an ultimate proof for the existence of a covalent (charge-transfer) component in hydrogen bonds.

